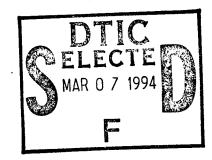
Design of a Laboratory Study of Contaminant Film Darkening in Space

1 October 1993



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CHARLES E. WHITED, Colonel, USAF Deputy Director of Program Management

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One of the most deleterious effects of spasilvered fused-silica thermal control mirror with precision. Here we discuss the design effect, as determined by the composition induced darkening. This effort includes for materials likely to be precursors of photos sensitivities to energetic irradiation in the spectra of photochemically deposited film with electrons, vacuum ultraviolet light, a have been chosen as analogs for major clistelection and a prioritization of their poteresults are also described.	ors or solar of a labor of the contain our major electronically of space environs on fused sond ions. Easses of spacential important	tell coveratory prominant from the ements: deposited comment; silica; and chof the eccraft cance. A	or slips. How ogram to entill and sub- the quantity decontaminal measurements and the measures ese elements ontaminants pparatus des	weve hance sequentative ant file ent of ureme s is d s is p sign	er, this effect can be the quantitative ent simulated ent e identification of lms; prediction of frates of deposi ents of further f liscussed. A set resented, include and performance	nnot currence understanding the class of these ration and cilm darket of organing the rate and ear	ently be predicted tanding of this ental radiation-sses of organic materials' optical absorption ening by irradiation ic materials that ationale for their ely experimental
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PREFACE

It is a pleasure to acknowledge the contributions of our many colleagues during the course of this work. Mr. Harry Newton converted our concept of the experimental apparatus into machine drawings. Much of the hardware was fabricated in The Aerospace Corporation machine shop and by the Chemistry and Physics Laboratory, Research Instrumentation and Computers Staff. Mr. Ross Hyman of Antioch College assisted in the initial apparatus assembly.

The laboratory data acquisition program was written by Mr. Mike Yao of the University of California, Berkeley. The CALCRT program was written by Prof. K. Palmer of Westminster College and supplied to us by Mr. W. T. Bertrand of ARVN/CALSPAN Corporation. The nonlinear least–squares fitting routine, entitled GASAUS, was written and supplied to us by Dr. H. J. Wertz of The Aerospace Corporation, Systems and Computer Engineering Division. Ms. Lynn Friesen and Mr. Kirk Crawford provided advice and assistance in the use of the VAX for data analysis.

Mr. B. A. Rockie and Mr. F. B. Sinsheimer of The Aerospace Corporation, Materials Sciences Laboratory, advised and assisted in the *ex situ* reflectance and ellipsometry measurements of the witness samples.

Dr. H. K. A. Kan and Mr. T. B. Stewart provided valuable technical discussions and advice. We also thank Mr. E. Simburger for continuing support and encouragement.

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I. INTRODUCTION

One of the most significant system impacts of spacecraft self-contamination is the "darkening" of optical or thermal control surfaces. In particular, the performance of fused silica second-surface thermal control mirrors and solar cell cover slips has been observed to be degraded by the effects of contaminant films.¹ In each case, the effect of the contaminant film is to absorb some fraction of the incident solar radiation.

The magnitude of this effect cannot be predicted with high reliability. This uncertainty has two primary origins: Spacecraft contaminant films are not made of pure, well characterized materials and, once deposited, they are subject to radiation-induced darkening by the components of the natural space environment.

This report presents the philosophy, design, and initial results of a program aimed at improving control of the optical effects of contamination in the design of a spacecraft. The goal of this work is to provide the basic data needed to produce criteria for the selection of spacecraft material based on the effects of the contaminant films they produce, not just the quantity of material they outgas.

The approach taken is threefold:

- A spacecraft nonmetallic materials list was analyzed to predict the sort of compounds that will outgas from these materials, becoming contaminant film precursors.
- The effects of the geosynchronous space environment on the various classes of outgassers were estimated.
- An experimental program has been undertaken to measure the optical properties of contaminant films from a list of model precursors, under simulated space environment conditions.

Section II presents the results of the spacecraft nonmetallic materials list analysis and radiation sensitivity estimates. Section III presents a rationale for simulation analysis of the potential effects of the geosynchronous environment on organic contaminant films. The remainder of the report describes the experimental portion of this project and presents some initial results.

II. MATERIAL SELECTION

As a starting point, a complete list of organic materials on a particular satellite, consisting of representative types of films, foams, wire insulation, etc., which were considered representative for satellites in general, was chosen for study (see Table 1). Of special interest was not the base material itself, but rather species that could outgas from the base material in space vacuum and condense on critical optical surfaces on the satellite, there to undergo photochemical deposition and radiation-induced darkening. Such species could consist of unpolymerized monomer, solvents, or catalysts used in polymerization reactions, and additives such as plasticizers and antioxidants, as well as other materials that result from polymer aging.

VCM (volatile condensable material) data were available for all materials on the list. However, in the vast majority of cases, only weight data were available with little, if any, data available on the chemical composition and structure of the VCMs. When the latter data were available, they were used directly. In other cases, the base material was considered along with additives employed during its manufacture to project the type of chemical species that could outgas from the base material. Also considered was thermal aging of the base materials. The latter, which consists of exposure of the base materials to high temperature for short periods of time, is thought to reasonably reflect the aging a base material would experience over a long term at orbital ambient temperatures. Moreover, since radiation exposures frequently yield results similar to thermal aging, radiation exposure of base materials was also considered. Here, as for thermal aging, the emphasis was not on changes in the base material itself, but rather in the types of VCMs that could be produced by these processes.

These various considerations yielded weights and probable chemical structures for VCMs from the base materials. This information was then used to estimate potential electron and proton space radiation effects on each material. There are several components of the estimate, the first of which is the bond strengths of the molecule. Examination of the various C-H, C-O, C-N, etc., bonds in a molecule can indicate which is the weakest and most likely to break upon irradiation. The second component is the functional groups that make up the molecule, as well as their relation to one another. This can affect not only the radiation stability of the molecule, but also the absorption spectrum of the outgassing material, as well as its radiation degradation products. An example is a material that contains benzene rings that are well known to lend some radiation resistance to the material (such structures may work in the opposite fashion with regard to darkening, however, particularly if they can trap electrons or lead to resonance stabilization of structures that absorb strongly in the ultraviolet and/or visible spectral regions.) Absorption of solar radiation by the VCMs was also considered, not only from the point of direct photolysis, but also from the point of synergistic interaction resulting from simultaneous particulate radiation. In all

cases, radiation-induced chemical changes likely to produce darkening were of primary interest.

The results of these exercises are shown in Table 2. The left column lists projected outgassing contaminants in order of decreasing importance with respect to their anticipated ability to produce darkened films when exposed to space radiation. The main sources of these contaminants for the satellite of interest are given in the second column of Table 2. The relative abundance, molecular structure considerations, and absorption spectra data were integrated with radiation degradation estimates to order the list in terms of anticipated relative contributions to darkening. The final column in Table 2 lists model contaminants for laboratory study. The latter materials were chosen on the basis of their similarity to actual anticipated contaminants, not necessarily on the basis of exact chemical structure, but rather with respect to their anticipated sensitivity to space radiation effects. Other considerations included appropriate vapor pressure ranges for ease of handling in the laboratory, and availability.

A detailed report of the literature review and other considerations that produced Table 2 is described in the appendix.

Table 1. Contractor-Supplied List of Materials

No.	Material	Weight (g)	TWL* (g)	VCM* (g)
1	Syntactic Foam	26183.794	230.417	7.855
2	PS727-1 Polysulfane	776.511	103.276	5.669
3	Kevlar	7990.400	291.650	2.397
4	Kapton	11259.200	96.829	2.252
5	Graphite Epoxy	7372.000	34.074	1.514
6	PIM-984 Epoxy 1	12212.600	54.957	1.221
7	Tape 3M X1157	37.822	2.372	0.950
8	RTV566	4308.510	8.617	0.862
9	Epoxy Fiberglass	15424.263	85.152	0.618
10	Polyimide PWB	5716.030	48.586	0.572
11	Stephan Foam G504	1110.619	6.997	0.444
12	EC3924 Primer	693.560	6.381	0.416
13	Uralane 5753	1105.115	8.068	0.332
14	Epoxy Adhesive	398.055	1.115	0.318
15	Uralane 5750	1323.764	11.517	0.265
16	Silicone	57.425	0.477	0.230
17	Epoxy Prepreg	722.650	5.348	0.217

^{*}As per ASTM E-595

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Table 1. Contractor-Supplied List of Materials (continued)

No.	Material	Weight (g)	TWL* (g)	VCM* (g)
18	Epiphen 825A	2091.578	16.314	0.209
19	FM 123	1975.004	15.998	0.198
20	Cotton Phenolic	312.338	1.249	0.187
21	Solithane 113	862.538	4.140	0.173
22	EC2216	284.971	2.337	0.171
23	Ablefilm 546	476.420	3.326	0.143
24	Velcro-Polyester	181.600	1.889	0.127
25	Epoxy Fillet	403.000	1.693	0.121
26	Dacron Tape	586.696	5.643	0.111
27	A-1177-B	443.478	1.996	0.089
28	Stathane 823	276.453	3.953	0.083
29	Chemglaze Z302	542.832	7.545	0.054
30	Diallylpthalate	444.686	1.956	0.044
31	Epoxy PWB	214.834	1.805	0.043
32	EP828-V125-MDA	68.025	0.286	0.041
33	Kynar Sleeve	56.921	0.221	0.040
34	Scotchcast 281	69.565	0.250	0.035
35	Chemglaze A276	100.378	1.134	0.031
36	966 Adhesive	272.400	2.778	0.027
37	Solithane 113/300	100.625	0.483	0.020
38	Mystic 7453	47.240	0.302	0.019
39	Strap-Nylon	23.672	0.092	0.017
40	Sleeving	48.833	0.249	0.015
41	Eccobond 57C	35.149	0.183	0.014
42	Ероху	5.750	0.066	0.012
43	Loctite A	10.200	0.558	0.011
44	Polysulfide	3.100	0.113	0.006
45	Epon 825/HV	58.696	0.311	0.006
46	Torque Stripe	76.839	0.087	0.005
47	FM41 Adhesive	52.124	0.245	0.005
48	Epon 828/V140	36.522	0.076	0.004
49	Warno Ink	6.075	0.280	0.003
50	Urethane Insulation	37.436	0.113	0.003
51	Tape 3M 1318	1.957	0.009	0.003

^{*}As per ASTM E-595

Table 1. Contractor-Supplied List of Materials (continued)

No.	Material	Weight (g)	TWL* (g)	VCM* (g)
52	PR1440 Polysulfane	1.078	0.052	0.003
53	Mylar Sleeving	8.725	0.054	0.003
54	Tape 3M 415	29.807	0.272	0.002
55	Tape 3M 27	1.957	0.040	0.002
5 6	Anodize	4.319	0.029	0.002
57	Q Dope	0.350	0.027	0.001
5 8	Polyimide Film	3.696	0.032	0.001
59	Epon 828/HV	7.146	0.038	0.001
60	Eccosorb CR124	5.088	0.006	0.001
61	DC6-1104	0.866	0.003	0.001
62	A-1777-B	7.561	0.034	0.001
63	Viton	166.585	0.266	0.000
64	TFE Wire Insulation	1964.854	0.197	0.000
65	TFE Wire	1327.120	0.133	0.000
66	TFE Sleeving	571.039	0.057	0.000
67	TFE Coax	5.566	0.001	0.000
68	Scotchweld 3501	0.017	0.000	0.000
69 [,]	PTFE Rod	13.101	0.001	0.000
70	Nylon 6/6	842.502	17.019	0.000
71	Nylon	607.720	12.276	0.000
72	Mylar Film	0.306	0.000	0.000
73	Hysol C-1	103.040	1.072	0.000
74	GR-Epoxy	9.680	0.023	0.000
75	FM24 Epoxy	2879.000	29.654	0.000
76	FEP Tubing	19.700	0.000	0.000
77	Epon 828 V140	2.525	0.005	0.000
78	Coax (Teflon)	0.204	0.000	0.000
7 9	Chemglaze Z	0.099	0.001	0.000
80	Barrier Coat	0.000	0.000	0.000
81	Armstrong A-12	0.255	0.001	0.000
82	Apiezon C	162.675	51.243	0.000

^{*}As per ASTM E-595

Table 2. Materials List

			Mo	lecular Struc	cture*	Absor	ption Spectra	<u>*</u>
Material	Sources	Abundance*	Bond Strengths	Functional Groups	Ionization Trapping	Solar Match	Absorption Strength	Model Contaminants
Phthlates	Polyester, Urethanes	Н	M	М	Н	M	M	Di(2-ethylhexyl) Phthalate
Phenols	Epoxies	н	M	H	H	M	M	4-Cumylphenol,
	_							4,4'-Isopropylidene Phenol
Polybenzimidizoles	Kapton	H	M	M	M	H	H	N-Phenylphthalimide
Aromatic Hydrocarbons	Many	н	M	M	Н	M	M	Bibenzyl, Dodecahydrotriphenylene
Aromatic Amines	Urethanes, Epoxies	L	L	M	Н	M	M	4-Tetradecylaniline
Silicones	Silicones	M	M	M	M	M	M	Methylphenylsiloxane
Alkenes	Many	M	H	L	L	L	L	Squalene, A-Humulene
Aliphatic Carbonyls	Many	M	M	M	L	L	L	10-Nonadecanone, Tetradecylaldehyde

^{*}High (H), Medium (M) or Low (L)

III. SIMULATED RADIATION ENVIRONMENT

Energy fluxes for solar² and particulate³ (averaged) radiation in the geosynchronous environment are given in Table 3. (Note that higher energy particles would contribute little.) Also given in Table 3 are estimated amounts of incident energy that would be absorbed and the chemical events caused by that energy absorption. These latter values were estimated assuming a 1000-Å film and a 10-molar concentration of absorbing species. Absorption coefficients in the near and mid-ultraviolet (UV) were taken as 10 and 300 l/mole cm, respectively, with quantum yields for photolysis (the fraction of absorbed photons that lead to molecular bond rupture) of 0.01. These values can vary considerably (± an order of magnitude) as a function of the particular molecule and wavelength of the UV photon.⁴ However, they are thought to represent reasonable average values for the species of interest here. For the far UV region, total absorption was assumed as well as a photolytic quantum yield of unity. Energy absorption from incident particles was estimated using published stopping powers, 5,6 while the number of chemical events was estimated assuming three chemical events per 100 eV of absorbed energy. The latter value is thought to represent a reasonable average for the materials of interest here, although actual values may vary by a factor of ± 3.7

Table 3 suggests that solar UV can generate the highest number of chemical events and should be simulated. This can be done with a high pressure Xe lamp for the near and mid UV and with a medium pressure Xe lamp for the far UV. Although visible and infrared (IR) radiation typically would be expected to do minimal direct photochemistry, they can contribute synergistically with particulate radiation and should ideally be simulated. The visible portion of the solar spectrum is reasonably well simulated by the high pressure Xe lamp. No attempt is made to simulate the solar IR since accelerated laboratory tests could lead to sample heating that would not actually occur in the space environment. Moreover, any synergisms resulting from IR exposures would more than likely also occur with visible exposures.

Although potential chemistry induced by electrons, protons, and oxygen ions appears significantly less than that resulting from simulated solar UV exposures, these radiations may contribute considerably more than their share to film coloration as they can continue to create damage deep within the film even if the outer layers of the film become opaque to solar UV radiations. Indeed, available evidence from the literature supports this conclusion. Moreover, particularly in the case of oxygen ions, these particles will come to rest within the film and can induce further chemistry. Consequently, these particles are to be simulated with a medium-energy electron flood gun ($\leq 5 \text{ keV}$), and an ion gun with an electrodeless plasma-ion source with mass filtering for O⁺ and H⁺ at energies up to 20 keV. (Both guns are manufactured by Kimball Physics, Inc.)

Table 3. Synchronous Space Radiation Fluxes and Potential Chemistry in a 100-nm Film.

		Energy Flux	<u>(μW/cm²)</u>	Chemical Events	
Radiation	Range	Incident	Absorbed	cm ⁻² sec ⁻¹ /10 ¹⁰	
Solar				,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	
Visible	400-700 nm	48,000	_	-	
Near UV	300-400 nm	12,000	0.28	50	
Mid UV	200-300 nm	1,600	1.1	140	
Far UV	<u>100–200 nm</u>	4.1	<u>4.1</u>	<u>500</u>	
Total	100–700 nm	61,604	5.5	690	
Electrons	0.1-5 keV	0.10	0.045	0.85	
	5-10 keV	0.12	0.005	0.10	
	10-15 keV	0.13	0.002	0.04	
	15-50 keV	1.1	0.004	0.07	
• N= :	50-100 keV	1.9	0.001	0.03	
	100-200 keV	3.3	<u>0.001</u>	0.02	
Total	0.1-200 keV	7.7	0.058	1.1	
Protons	0.1-5 keV	0.002	0.002	0.04	
	5-10 keV	0.006	0.004	0.08	
	10-15 keV	0.01	0.005	0.09	
	15-50 keV	0.13	0.038	0.72	
	50-100 keV	0.16	0.023	0.43	
	100-200 keV	0.17	0.010	0.19	
	200-800 keV	0.25	<u>0.005</u>	<u>0.09</u>	
Total	0.1-800 keV	0.74	0.087	1.6	
Oxygen Ions	0.1-5 keV	0.001	0.001	0.02	
	5-10 keV	0.003	0.003	0.05	
	10-15 keV	0.004	0.004	0.08	
	15-50 keV	0.058	0.058	1.1	
	50-100 keV	0.069	0.067	1.3	
	100-200 keV	0.069	0.044	0.82	
	200-800 keV	0.11	<u>0.015</u>	<u>0.29</u>	
Total	0.1-800 keV	0.31	0.19	3.7	

IV. EXPERIMENTAL

A. APPARATUS

Figure 1 shows a schematic representation of the major elements of the contamination effects apparatus assembled for this program. There are three functional levels of the experiment. The middle plane is the deposition plane at which the target is exposed to an organic effluent and vacuum ultraviolet (VUV) photons. The upper plane is for irradiation of a previously deposited film by electrons, ions, and photons. At the lower plane the transmission spectrum of the film is measured using a Cary 14 spectrophotometer. Major elements of the experimental setup are described in more detail below.

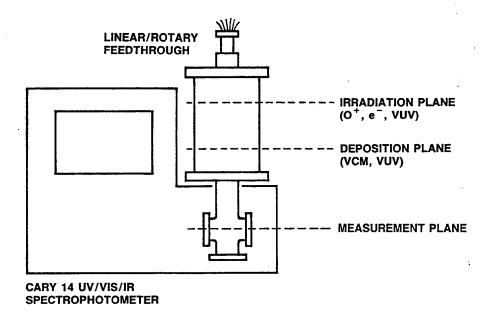


Figure 1. Schematic Representation of the Photochemical Deposition and Contaminant Effects Apparatus.

1. VACUUM CHAMBER AND MANIPULATOR

The three experiment "planes" are contained within a stainless steel vacuum chamber equipped with crushed copper seals, which is evacuated by a 350 liters/sec turbomolecular pump. The chamber is lined with a copper shroud that is conductively cooled by a liquid nitrogen reservoir. Openings in the shroud permit the molecular, light, and particle beams to illuminate the sample.

An appendage to the vacuum chamber extends into the sample compartment of the spectrometer. Sapphire windows on this appendage permit the spectrometer's light beam to pass through the chamber, with an effective wavelength range of 210 – 2500 nm.

A linear/rotary manipulator is provided to move the film and witness samples among these various planes. Approximately 1 m of translation is provided. The manipulator is essentially a smooth tube mounted on a dovetail lead screw assembly (Velmex Unislide). The vacuum seal is made by passing the tube through three spring-loaded Teflon[®] seals (Fluorocarbon Co., Mechanical Seals Division). The two spaces between the three seals are "differentially pumped" by mechanical vacuum pumps to reduce the effective leak rate into the chamber. A wiring harness (Pave Technology, Inc.) is fed through the translator tube for the sample monitors (temperature sensors and QCM) and for the sample temperature controller.

The base pressure of the vacuum system empty is less than 10^{-8} Torr. Operating pressures are typically 2×10^{-8} Torr with all experiment elements installed and operating.

2. TEST FIXTURE AND WITNESS SAMPLES

Figure 2 shows a photograph of the deposition samples. A temperature-controlled quartz crystal microbalance (TQCM) is used to monitor the accumulation of mass on the sample. The crystals used in this experiment are 10-MHz doublets, which have two vapor-deposited aluminum electrode pairs. One electrode pair serves as a reference and is shielded from the contaminant source by a sapphire window. The other electrode pair is left unshielded.

A hybrid oscillator/mixer circuit (QCM Research, Inc.) is used to drive the two electrode pairs and to generate the beat frequency of the two oscillators. The change in beat frequency is proportional to deposit mass load by the factor 4.43×10^{-9} g cm²Hz⁻¹.

Two "witness samples" (0.25-in. diam) are included. Typically, one is a polished silicon disc and the other is an SiO_X coated aluminum mirror (Melles-Griot). These samples are used for ex situ measurements of film properties by ellipsometry and for characterizing the reflectance and scatter properties of the final film. Finally, there is a fused silica plate (Corning 7940, Optical Coating Laboratories, Inc.). This is the substrate for film transmission measurements.

The temperature of the samples and TQCM is actively controlled by a thermoelectric heater/cooler (TED). The temperature of the TQCM is monitored by a thermocouple bounded directly to its surface. Another thermocouple monitors the temperature of the heat sink for the TED, which is also the heat sink for the QCM oscillator circuit. The heat sink temperature is stabilized by circulating water through it.

3. PHOTOCHEMICAL DEPOSITION EQUIPMENT

Figure 3 shows a schematic representation of the deposition plane. The chamber is built to accommodate two contaminant sources and two light sources on the deposition plane.

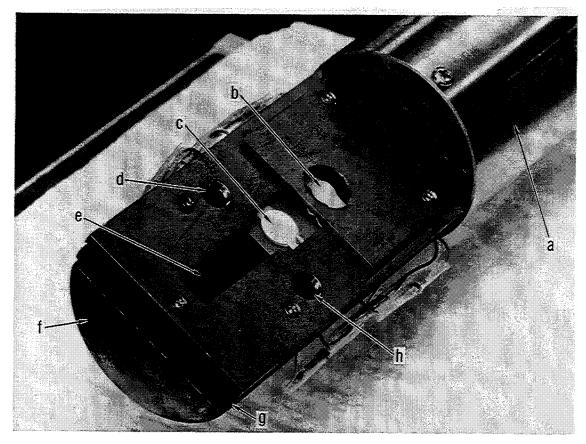


Figure 2. Deposition Test Fixture:

- a. Oscillator circuit and electrical connector housing: A standard QCM Research oscillator chip is used in this device. The vent for the electronics housing and cable harness is not shown. It is on the back side so that it is directed to the cryoshroud, away from the samples and QCM.
- b. QCM reference crystal, masked by a sapphire disk: The QCM uses a doublet crystal, one with two sets of electrodes plated on one quartz crystal. Aluminum electrodes are used. The red and white thermocouple on the crystal is just visible under the edge of the mask.
- c. QCM sense crystal.
- d. Silicon witness sample: A polished disk of silicon, 0.2-in. diameter, is used as a witness sample for ex situ analysis of film properties. The primary use of this witness sample is for ellipsometery to provide independent measurements of film thickness and index of refraction at two wavelengths, in the visible spectrum.
- e. Fused silica (SiO₂) sample: Corning 7940 fused silica, obtained from Optical Coatings Laboratory, Inc., is used as the witness sample for the *in situ* transmission measurement. This is the material specified for the standard thermal control mirror used on spacecraft.
- f. Heat sink: The heat sink and thermostat block each have oblong holes which match the fused silica sample, to permit passage of the Cary 14 light beam.
- g. Thermostat block: The thermostat block is pressed against the active surface of the TED used for temperature control.
- h. SiO_x/aluminum mirror witness sample: The primary use of this witness sample is for *ex situ* measurement of film scatter in the visible spectrum. Individual mirrors are characterized for total reflectance and scatter at 630 nm before use.

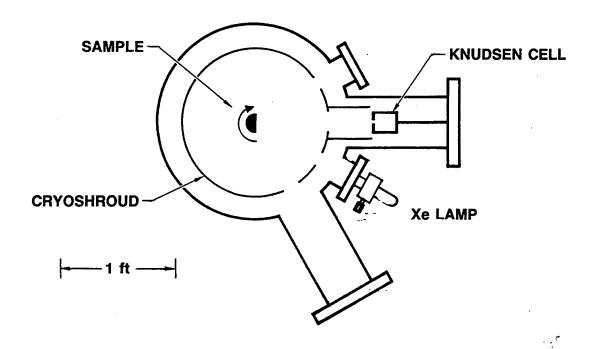


Figure 3. Schematic Representation of the Deposition Plane of the Experimental Apparatus.

An effusive beam source (Knudsen cell) provides a constant flow of the contaminant analog material to the deposition fixture. The source, a simple copper can with a round orifice, is mounted to a thermostatically controlled heat sink. For bis-diethylhexylphatate (DEHP), a source temperature of about 340 K was appropriate. A "flag" mounted on a rotary feedthrough can be used to interrupt the flow to the deposition fixture. An extension of the cryoshroud into the beam source side-arm provides collimation of the contaminant beam to about 1.5 in. in diameter at the deposition fixture. For a purely effusive beam, this corresponds to uniformity of about 10% across-the full exposed area.

The contaminant film is irreversibly deposited by the action of VUV light. Simple microwave-excited, sealed rare-gas resonance lamps are used. The lamps are excited at 2450 MHz by a 1/4 wave foreshortened cavity of the Evenson design. For the experiments reported here, the lamp was filled with ~200 Torr of Xe, to produce a broad emission spectrum from 150-180 nm⁴, with an integrated intensity comparable to the sun's in this wavelength region.

4. SPECTROMETER AND INTERFACE

The spectrometer is a dual beam device dedicated to this project. Ultraviolet and visible spectra are measured with a photomultiplier tube detector and a hydrogen lamp or quartz/halogen lamp, respectively. A lead sulfide (PbS) detector and tungsten lamp are used in the near infrared. The spectrometer is configured to measure transmission.

A commercial device, the LUSI 3 (Spectra Instruments), replaces some of the tube electronics in the Cary 14, corrects the raw transmission data for light source and detector variations, and provides a serial data stream of the measured spectrum.

5. DATA ACQUISITION

An IBM AT® computer continuously collects sample quartz-crystal microbalance beat-frequency and, upon request, collects the data stream from the spectrometer. A variety of peripheral devices are used to collect or transmit data. All data are stored on the computer's hard disk. (See Figure 4.) For analysis, data are transferred to a Digital Equipment Corporation VAX computer.

B. RESULTS

1. PHOTOCHEMICAL DEPOSITION

Photochemical deposition of the contaminant film was accomplished in a manner similar to that described in earlier experiments. 1,9 Care was taken to ensure that there was no steady-state film deposition in the absence of either the DEHP flow or VUV irradiation. Figure 5 shows a plot of the TQCM frequency over the roughly 4-week period during which the film was deposited and transmission spectra were measured. Also shown is a synchronized plot of TQCM temperature. The occasional spikes in the TQCM temperature, with corresponding spikes in the frequency, occur when the test fixture is moved out of the field of view of the cryoshroud to measure the transmission spectrum.

2. ABSORPTION SPECTRA

Fifteen measurements of the UV and visible spectra were taken during the course of film deposition. The film thickness at each time of measurement was calculated from the change in beat frequency, from the beginning of the experiment, assuming that the film density is equal to the liquid density of the starting material.

Transmission spectra showed broad, monotonically increasing absorption from 700 – 220 nm, with a hint of some structure visible in the near UV. Figures 6 and 7 show two typical spectra. For comparison, a spectrum of the starting material is shown in Figure 8.¹²

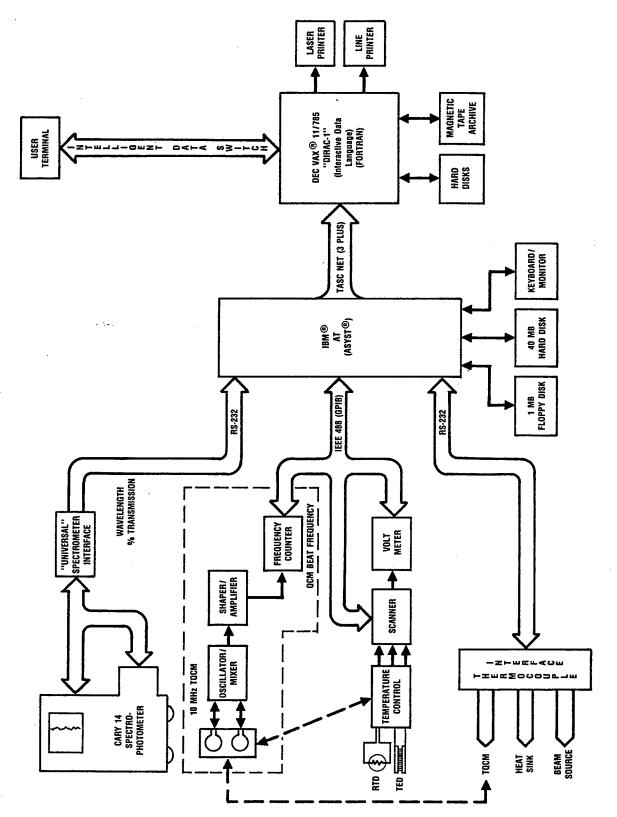


Figure 4. Schematic Representation of Experimental Data Acquisition and Analysis Flow.

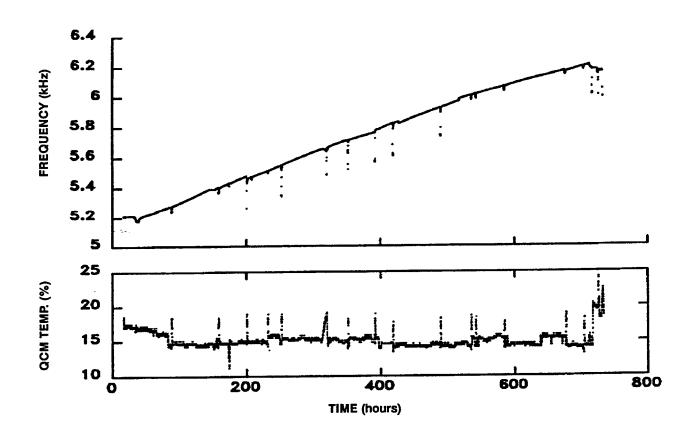


Figure 5. (Top) Quartz-Crystal Microbalance Beat Frequency during Photochemical Deposition and Transmission Spectrum Acquisition. See text for details. (Bottom) Synchronized Plot of Quartz Crystal Microbalance Temperature.

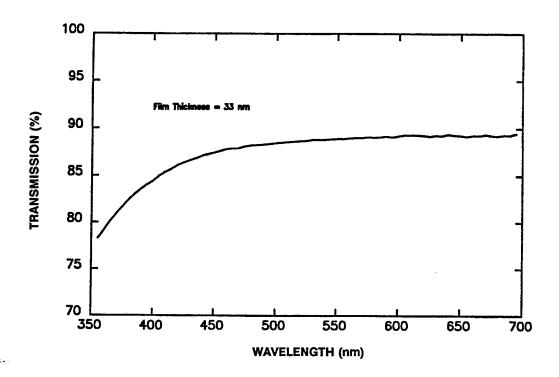


Figure 6. Typical Visible and Near Ultraviolet Transmission Spectrum of Photochemically Deposited Film from DEHP Precursor. The film thickness was approximately 33 nm.

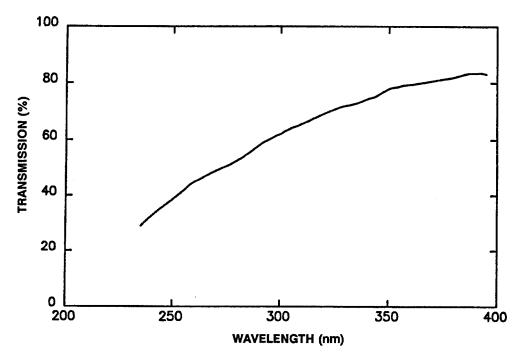


Figure 7. Typical Ultraviolet Transmission Spectrum of Photochemically Deposited Film from DEHP Precursor. The film thickness was approximately 33 nm.

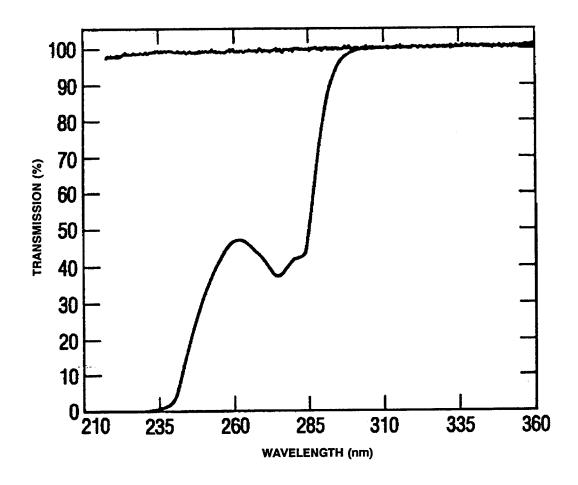


Figure 8. Transmission Spectrum of Virgin DEHP.¹³

3. WITNESS SAMPLES

Five sorts of ex situ measurements on the samples were performed: reflectance of the 7940 silica plate, transmission scatter of the 7940 silica plate, reflectance of the witness mirror, reflectance of the silicon witness sample, and ellipsometry of the silicon witness sample. All measurements were performed with helium-neon laser sources at 632.8 nm. The results of these measurements are summarized in Table 4.

From these measurements, and the absorptance which can be inferred from them, a complex index of refraction of the film at 632.8 nm can be chosen. Figures 9-11 summarize this process. In each case, the experimental observable is plotted, and the property modeled by various choices of n and k plotted by a series of lines. The bold line corresponds to a choice of n=1.6, and k=0.01, which describes the data well.

Table 4. Results of Ex-Situ Analysis of Witness Samples (all measurements at 632.8 nm)

Sample	Transmission*	Transmission* Reflectance (specular/diffuse) (total/diffuse)		Phase
	(%)	(%)	(degr	rees)
SiO ₂				
Initial	/0.3	6.4/0.3		
Final	/0.5	7.6/0.9		
	90.5 ± 0.5 /			
	/0.3	7.4/0.3		
Silicon				
Initial		35.1/0.2	10.4	170.
Final		24.1/0.5	22.945	89.167
		23.3/0.4	22.943	89.188
Al Mirror				
Initial		87.0/0.2		
Final		85.1/0.7		
		85.4/0.4		

^{*}Transmission scatter baseline = 0.2 - 0.3%

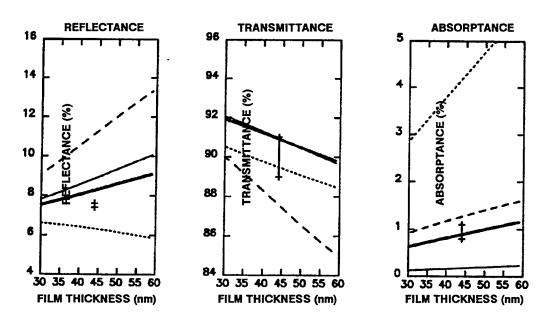


Figure 9. Observable Optical Properties of the Final DEHP Film on Fused Silica.

Plusses: Experimental data Dashed line: Calculation for $\hat{n} = 1.770 + 0.014i$

Solid line: Calculation for $\hat{n} = 1.646 + 0.002i$

Wavelength = 633 nm (HeNe laser). Bold line: Calculation for $\hat{n} = 1.6 + 0.01i$ Dotted line: Calculation for $\hat{n} = 1.294 + 0.057i$

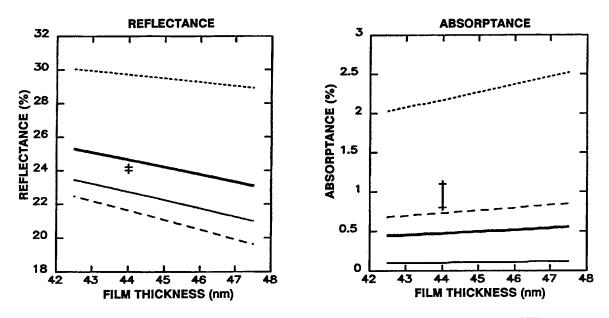


Figure 10. Observable Optical Properties of the Final DEHP Film on Silicon.

Plusses: Experimental data

Dashed line: Calculation for $\hat{n} = 1.770 + 0.014i$

Solid line: Calculation for $\hat{n} = 1.646 + 0.002i$

Wavelength = 633 nm (HeNe laser). Bold line: Calculation for $\hat{n} = 1.6 + 0.01i$ Dotted line: Calculation for $\hat{n} = 1.294 + 0.057i$

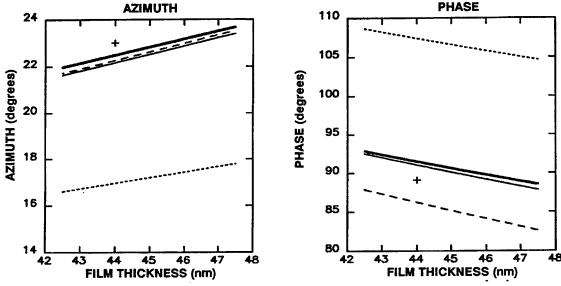


Figure 11. Ellipsometric Angles for the Final DEHP Film on Silicon.

Plusses: Experimental data

Dashed line: Calculation for $\hat{n} = 1.770 + 0.014i$

Solid line: Calculation for $\hat{n} = 1.646 + 0.002i$

Wavelength = 633 nm (HeNe laser).

Bold line: Calculation for $\hat{n} = 1.6 + 0.01i$

Dotted line: Calculation for $\hat{n} = 1.294 + 0.057i$

V. DATA ANALYSIS

A. TRANSMISSION MODEL

The transmission vs thickness data were analyzed by assuming that the film thickness is small compared to the coherence length of the source, while the substrate is thick compared to the coherence length. The real part of the substrate index was taken from a published dispersion curve appropriate to Corning 7940.¹³ The imaginary part of the index of the substrate was taken to be zero over the wavelength range of interest.¹⁴ (See experimental section.) The transmission of the film/substrate system was computed using a FORTRAN routine entitled CALCRT.

B. FITTING PROCEDURE

A least-squares fitting routine entitled GASAUS was used to fit the transmission vs. thickness data to obtain wavelength dependent values of the complex index. Derivatives of the variance of the fit with respect to the two parameters were calculated by finite difference. Data were fit every 5 nm, beginning at the short wavelength end of the visible data sets, and every 2.5 nm, beginning at the long wavelength end of the ultraviolet data sets.

The initial value of n was chosen in the range of 1.5 and 1.8. The fitting constraint on n was that it could not vary more than a factor of 2 (up or down) from the initial guess, at any wavelength. The extinction coefficient was constrained to lie between 0.00001 and 1. The fitting of the data proceeded upward or downward in wavelength from the starting point, with the initial guesses of n and k at the next wavelength being the best fit obtained at the previous wavelength.

C. RESULTS

The transmission vs wavelength fits were reasonably stable in the ultraviolet, where absorption was strong. However, in the visible, where the total change in transmission was only a very few percent, this was not the case. In the absence of other data, it would not be possible to make any statement about the values of n and k in the red end of the spectrum because of the instability of the fits in that wavelength range. However, the ex situ analysis of the witness samples has provided one point to "peg down" the variable end of these curves.

Figure 12 shows a set of n and k values chosen by smoothing the fitted data and adjusting the red end of the curves to agree with the $\hat{n}=1.6+0.01i$ value inferred from the witness samples. This adjustment amounted to a 10% change in the n value and a 30% change in the k value from the fit which most closely agreed with the index gleaned from the

witness sample analysis. Also shown in Figure 12 is a set of refractive index and extinction coefficient values often used to approximate the effects of spacecraft contaminant films. ^{15,16} The photodeposited DEHP film appears to be more strongly absorbing over a wide range in the visible and ultraviolet than this canonical spectrum.

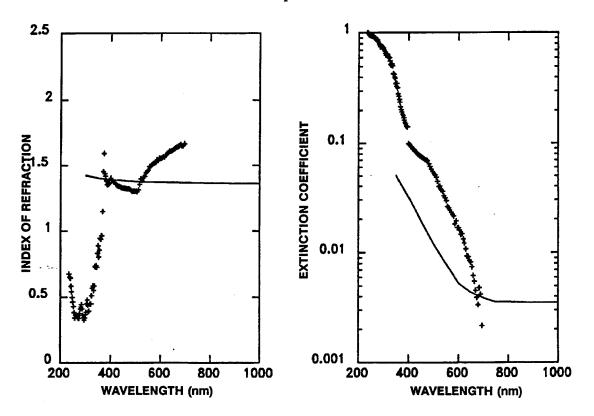


Figure 12. Comparison of Inferred Complex Index of Refraction of Photochemically Deposited DEHP with that Calculated by Zeiner from Laboratory and Flight Measurements of a Variety of Contaminated Surfaces: (left) index of refraction; (right) extinction coefficient.

VI. DISCUSSION

This report has presented the initial results of a laboratory program directed at developing the knowledge needed for effects-based materials selection guidelines for contamination control. The approach is threefold:

- A spacecraft nonmetallic materials list was analyzed to predict the sort of compounds that will outgas from these materials, becoming contaminant film precursors.
- The effects of the geosynchronous space environment on the various classes of outgassers were estimated.
- An experimental program has been undertaken to measure the optical properties of contaminant films from a list of model precursors, under simulated space environment conditions.

The initial experimental results of this project are promising, in that they show that the hardware is working, the data are analyzable, and (admittedly based on only one set of measurements) a contaminant precursor predicted to produce dark films did indeed do so. Of course it is not possible to draw any global conclusions on the basis of such a set of measurements about the role of chemical identity of the precursor in governing the optical properties of a photochemically deposited film. More measurements, including charged particle irradiation, from among the proposed list of precursors are needed, and are currently in progress.

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APPENDIX

Material Selection for Contamination Studies

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The contractor-supplied list of materials provided herein is examined with regard to the chemical composition of the base material and the solvents, catalysts and accelerators used in its production. Thus data are combined with outgassing information (where available) as well as accelerated thermal and radiation aging studies to arrive at the most likely materials that will outgas from the base material. In this context thermal and radiation (accelerated) aging studies are thought to reasonably reflect changes that will occur in materials under long-term aging under ambient conditions. Thus they are considered to reflect bond rupture that will occur long-term that will lead to generation of low molecular weight materials that can outgas from the base material.

Once potential outgassing materials have been identified, additional criteria are involved to arrive at a radiation sensitivity with regard to radiation-induced darkening of the outgassed material. The first and most obvious consideration is the amount of VCM (volatile condensable material) as indicated on the contractor-supplied list. This is by no means a clear indication of which materials will produce the most darkening, since a high VCM material may produce minimal darkening while a low VCM material may produce considerable darkening.

A second consideration is that of the molecular structure of the outgassing material. There are several components, first of which is the bond strengths of the molecule. Examination of the various C-H, C-O, C-N, etc., bonds in a molecule can indicate which is the weakest and most likely to break upon irradiation. The second component is the functional groups that make up the molecule, as well as their relation to one another. This can affect not only the radiation stability of the molecule, but the absorption spectrum of the outgassing material as well as its radiation degradation products. An example is a material that contains benzene rings that are well known to lend some radiation resistance to the material (such structures may work in the opposite fashion with regard to darkening, however, particularly if they can trap electrons or lead to resonance stabilization of structures that absorb strongly in the UV and/or visible spectral regions, a third component of this consideration.)

The final consideration is the absorption spectrum of the outgassing material and its potential radiation products. Do these spectra overlap strongly or weakly with solar spectrum? Strong overlaps suggest increases in potential photochemistry as well as solar absorptance. Of course, the spectral overlap must be combined with the absorption strength to ultimately determine the potential photochemistry and darkening.

All of these factors were considered in evaluating the contractor-supplied list of materials. In some cases, considerable information was available, and reasonably well defined potential outgassing materials and radiation darkening could be estimated. In other cases, sparse data were available and best "guesstimates" had to be made. One important consideration is that many of the materials considered are proprietary in nature. While general information was supplied, exact formulations were not necessarily provided. However, within these constraints, the various manufacturers and contractors provided sufficient information (which we gratefully acknowledge) that we feel will facilitate assessment of the materials and potential darkening that can occur.

The materials considered in this study are lisited in Table A-1, in order of decreasing VCM. Following Table A-1 are data sheets for the materials listed, starting with the highest VCM materials and progressing to the lower VCM materials. A description of the data sheets follows:

- A. Material: The number and descriptive name of the material as quoted in Table A-1.
- B. Specification: Material and/or mil spec code.
- C. System VCM: Values taken from Table A-1.
- D. Use: Typical uses for the material.

E. Chemical Information:

- Structure: Chemical structure of the base material. Also given, where relevant, are solvents or other key materials
 used during production of the base material that may be occluded in the material during production and later serve
 as a source of VCMs.
- 2. Curing Agent/Hardener/Catalysts: Materials used in conjunction with the base material to give a finished product, e.g., catalysts used with a polymer resin to produce a finished coating or potting compound.
- 3. Additives: Materials added to alter the properties of the base material, e.g., cabosil glass spheres to produce a syntactic foam, or to protect the base material such as antioxidants.
- 4. Fillers: Generally inert materials of low volatility such as graphite fibers, glass microspheres, or mica.
- F. Outgassing (Species Characterization): Where available, data are given for species characterized from ambient or near ambient temperature outgassing of the base material and/or finished product. Of particular interest are outgassing products that could condense on spacecraft surfaces and undergo darkening when subjected to UV and/or ionizing radiation. Thus, while most materials outgas H₂O and CO₂ (generally the largest outgassing species), these are of considerably less interest than, say, a high molecular weight organic molecule that could condense and discolor when irradiated. The various subheadings in this section refer to the analytical technique(s) used to make the measurements. These include: (1) GC/MS (gas chromatography and/or mass spectrometry), (2) IR (infrared spectroscopy), (3) UV (ultraviolet spectroscopy), and (4) HPLC/GPC (high-performance liquid chromatography or gel permeation chromatography).
- G. Degradation/Decomposition: In many instances ambient temperature outgassing data simply do not exist for the materials of interest. It is generally believed that exposing materials to high temperatures for short time periods will produce results similar to those obtained over longer exposures at ambient temperatures. This generally accepted principle of "thermal aging" is used extensively throughout the polymer industry. While the correlations between results of thermal aging and long-term ambient temperature aging may not necessarily be one to one, due to long-term relaxation processes that can occur in polymers that could affect chemistry, the correlations should be sufficient to provide qualitative and possible semi-quantitative information about outgassing products. Consequently, where available, thermal aging data are used to identify potential outgassing products. The key focus in this section is not changes in the properties of the base material, but rather the outgassing products.

Likewise, many studies have shown reasonable agreement between thermal aging and radiation-induced effects. Thus, in a sense, radiation exposure may be thought of as another form of accelerated aging. Where available, radiation data have been used to identify potential outgassing products. Again, the reader should keep in mind that the radiation data were examined here for the purpose of identifying potential outgassing products and <u>not</u> to assess radiation damage to the base material or the outgassed products.

In surveying the literature for thermal aging or radiation data, emphasis was placed on studies carried out in vacuum or inert gas atmospheres, since aging in an air environment can produce drastically different results in terms of potential outgassing products.

- H. Summary (Most Probable Outgassing Products): The emphasis was, based on the data in the preceding sections, to identify the most probable outgassing products that could condense on a spacecraft surface and undergo radiation-induced darkening. Thus, for example, species such as water, carbon dioxide, hydrogen, etc., that will not condense, or will give minimal radiation-induced darkening, are not considered here.
- I. Radiation Sensitivity (Darkening): Given the materials identified in section H and their potential for radiation-induced darkening (see text), an assessment is given for potential radiation-induced darkening. The descriptions used in this section are defined, for example, as: Low-minimal darkening or darkening confined to shorter wavelengths in the UV; moderate low level darkening across the solar spectrum or higher level darkening confined to the UV up to the UV/visible division (400 nm); high-high level darkening extending beyond the UV well into the visible portion of the solar spectrum.

Table A-1. Contractor-Supplied List of Materials

No.	Material	Weight (g)	TWL* (g)	VCM* (g)
1	Syntactic Foam	26183.794	230.417	7.855
2	PS727-1 Polysulfane	776.511	103.276	5.66 9
3	Kevlar	7990.400	291.650	2.397
4	Kapton	11259.200	96.829	2.252
5	Graphite Epoxy	7372.000	34.074	1.514
6	PIM-984 Epoxy 1	12212.600	54.957	1.22
7	Tape 3M X1157	37.822	2.372	0.950
8	RTV566	4308.510	8.617	0.862
9	Epoxy Fiberglass	15424.263	85.152	0.618
10	Polyimide PWB	5716.030	48.586	0.572
11	Stephan Foam G504	1110.619	6.997	0.444
12	EC3924 Primer	693.560	6.381	0.416
13	Uralane 5753	1105.115	8.068	0.332
14	Epoxy Adhesive	398.055	1.115	0.318
15	Uralane 5750	1323.764	11.517	0.265
16	Silicone	57.425	0.477	0.230
17	Epoxy Prepreg	722.650	5.348	0.217
18	Epiphen 825A	2091.578	16.314	0.209
19	FM 123	1975.004	15.998	0.198
20	Cotton Phenolic	312.338	1.249	0.187
21	Solithane 113	862.538	4.140	0.173
22	EC2216	284.971	2.337	0.17
23	Ablefilm 546	476.420	3.326	0.143
24	Velcro-Polyester	181.600	1.889	0.127
25	Epoxy Fillet	403.000	1.693	0.121
26	Dacron Tape	586.696	5.643	0.111
27	A-1177-B	443.478	1.996	0.089
28	Stathane 823	276.453	3.953	0.083
29	Chemglaze Z302	542.832	7.545	0.054
30	Diallylpthalate	444.686	1.956	0.044
31	Epoxy PWB	214.834	1.805	0.043
32	EP828-V125-MDA	68.025	0.286	0.041

^{*}As per ASTM E-595

Table A-1. Contractor-Supplied List of Materials, continued

No.	Material	Weight (g)	TWL* (g)	VCM* (g)
33	Kynar Sleeve	56.921	0.221	0.040
34	Scotchcast 281	69.565	0.250	0.035
35	Chemglaze A276	100.378	1.134	0.031
36	966 Adhesive	272.400	2.778	0.027
37	Solithane 113/300	100.625	0.483	0.020
38	Mystic 7453	47.240	0.302	0.019
39	Strap-Nylon	23.672	0.092	0.017
40	Sleeving	48.833	0.249	0.015
41	Eccobond 57C	35.149	0.183	0.014
42	Epoxy	5.750	0.066	0.012
43	Loctite A	10.200	0.558	0.011
44	Polysulfide	3.100	0.113	0.006
45	Epon 825/HV	58.696	0.311	0.006
46	Torque Stripe	76.839	0.087	0.005
47	FM41 Adhesive	52.124	0.245	0.005
48	Epon 828/V140	36.522	0.076	0.004
49	Warno Ink	6.075	0.280	0.003
5 0	Urethane Insulation	37.436	0.113	0.003
51	Tape 3M 1318	1.957	0.009	0.003
52	PR1440 Polysulfane	1.078	0.052	0.003
53	Mylar Sleeving	8.725	0.054	0.003
54	Tape 3M 415	29.807	0.272	0.002
55	Tape 3M 27	1.957	0.040	0.002
56	Anodize	4.319	0.029	0.002
57	Q Dope	0.350	0.027	0.001
58	Polyimide Film	3.696	0.032	0.001
59	Epon 828/HV	7.146	0.038	0.001
60	Eccosorb CR124	5.088	0.006	0.001
61	DC6-1104	0.866	0.003	0.001
62	A-1777-B	7.561	0.034	0.001
63	Viton	166.585	0.266	0.000
64	TFE Wire Insulation	1964.854	0.197	0.000
65	TFE Wire	1327.120	0.133	0.000

^{*}As per ASTM E-595

Table A-1. Contractor-Supplied List of Materials, continued

No.	Material	Weight (g)	TWL* (g)	VCM* (g)
66	TFE Sleeving	571.039	0.057	0.000
67	TFE Coax	5.566	0.001	0.000
68	Scotchweld 3501	0.017	0.000	0.000
69	PTFE Rod	13.101	0.001	0.000
70	Nylon 6/6	842.502	17.019	0.000
71	Nylon	607.720	12.276	0.000
72	Mylar Film	0.306	0.000	0.000
73	Hysol C-1	103.040	1.072	0.000
74	GR-Epoxy	9.680	0.023	0.000
75	FM24 Epoxy	2879.000	29.654	0.000
76	FEP Tubing	19.700	0.000	0.000
77	Epon 828 V140	2.525	0.005	0.000
78	Coax (Teflon)	0.204	0.000	0.000
79	Chemglaze Z	0.099	0.001	0.000
80	Barrier Coat	0.000	0.000	0.000
81	Armstrong A-12	0.255	0.001	0.000
82	Apiezon C	162.675	51.243	0.000

^{*}As per ASTM E-595

- A. Material: 1. Syntactic Foam
- B. Specification:
- C. System VCM (g): 7.855
- D. Use: Electrical casting and encapsulation.
- E. Chemical Information:
 - Structure Diglycidyl ether of Bisphenol A (DGEBA, Epon 815)
 - 2. Curing Agent/Hardener/Catalysts: Triethylenetetramine (TETA); HN951
 - 3. Additives: Cabosil (sodium silicate)
 - 4. Fillers: Glass microspheres or glass microballoons (GMB)
- F. Outgassing (Species Characterization):
 - 1. GC/MS: Principally H_2O , CO_2 , CO_3 , at 25-150°C (Refs. BR067A, VAS78A, SAN85A).
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.: Low molecular weight phenols from HPLC of Bisphenol-A (Ref. SZA78A).
- G. Degradation/Decomposition:
 - Thermal/Aging: Volatile products included H₂O, CO, CH₃OCH₃, CH₂= CHCH₂OH, CH₂CHCHO, CH₂=CH₂, CH₃CH=CH₂, phenol, substituted phenols, aromatic esters with carbonyls and or ethylenic groups (280°C), (Refs. GRA85A, GRA85B, GRA86A).
 - 2. Radiation
 - a. Ionizing: UV and IR studies of electron irradiated material gave results consistent with thermal/aging studies. Carbonyl and ethylenic bonds were formed, as well as aromatic free radicals (Refs. BUR80A, BUR82A).
 - b. UV: Similar to thermal/aging with addition of ${\rm H}_2$ and aromatic hydrocarbons (Refs. GRA85C, GRA86B).
 - c. VUV
- H. Summary (Most Probable Outgassing Products): Outgassing products of principle concern with regard to potential radiation darkening are the phenols and substituted aromatic esters and to a lesser extent the carbonyl containing species and unsaturated hydrocarbons.
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 2. PS727-1 Polysul
- B. Specification:

Also: MIL-S-8516E

- C. System VCM (g): 5.699
- D. Use: Potting and sealing; insulation of electric/electronic components.
- E. Chemical Information:
 - 1. Structure: Mercapton terminated long chain aliphatic polym. containing disulfide linkages. Thiol gps. oxidized with curing agents.
 - A. Polysulfide.

Mix Ratio: 100 pts. A + 10 pts. B.

- 2. Curing Agent/Hardener/Catalysts: B. Accelerator (cntns Pb): Mn0, $Pb0_2$, Dichromates or org. free radicals. Thermal stability: $Cr_2O_7 >$.
- 3. Additives: Mn0 > Pb0₂
- 4. Fillers: Silicon dioxide (325 mesh).
- F. Outgassing (Species Characterization): Product may contain residual mercaptides?
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition: Hazardous decomposition produces: CO, CO₂, SO₂, low m.w. HC's, HS (with burning).
 - 1. Thermal/Aging: Thiol content decreases with aging due to cross-linking and production of higher m.w. comp(s). GC/MS (Pyrolysis) at 358 and 485°C shows four major peaks: 1,3 oxathiolane, 2-mercapto methyloxirane, 1,3 dioxathiocone and 1,3 dioxa 6,7 dithionane (cyclic monomer formed by a single mechanism.

IR/Titration show that thiol content decreases with aging. SH concentration and m.w. have only a marginal effect on decomposition products. decomp. is not end initiated but predominantly random.

Only the cyclic monomer is observed at approx. 130°C thiol termin. LP undergo cyclodeployment on steam or dry distillation.

Degrad. is initiated by homolytic cleavage of C-X bonds; resulting in radical formation leading to a complex mixture of products. C-O (formal bond) decomp. is observed in air. Liquid polysulfides decompose by ionic or free radical processes (depending on temp).

Decomp. Products: CO_2 , C_2H_4O , CS_2 , C_2H_4S , $C_6H_{14}O$ (ethylisobutyl ether, vinyl mercaptide.

- 2. Radiation
 - a. Ionizing
 - b. uv
 - c. VUV
- H. Summary (Most Probable Outgassing Products):
- I. Radiation Sensitivity (Darkening):

- A. Material: 3. Kevlar (49)
- B. Specification:
- C. System VCM (g): 2.397
- D. Use: Aerospace: Structural, high performance fibrous epoxy composite.
- E. Chemical Information: Fully aromatic polyamide (Aramid fibres).
 - 1. Structure: A. Resin: Novolac epoxy (polyglycidalether of a phenol formaldehyde, 48.2% by weight).
 - B. Aromatic polyamide (Poly [p. phenylene terephthalamide, PPTA], 51.8% by weight). (Ref. MCF78A)
 - Curing Agent/Hardener/Catalysts: Undetermined; however, in all probability the catalyst is an amine which reacts with the epoxide or hydroxide group of the epoxy.
 - 3. Additives:
 - 4. Fillers: Aramid fibers.
- F. Outgassing (Species Characterization):
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - Thermal/Aging: H₂O and CO₂ and above 200°C, aliphatic esters and alcohols, acetone, xylenes, benzene, toulene, phenol and substituted phenols (Refs. LUM81A, LUM82A, END86A).
 - 2. Radiation
 - a. Ionizing: Similar products to thermal aging with the addition of low molecular weight aliphatic hydrocarbons olefine and aldehydes. Considerably higher number of species observed (END86A).
 - b. UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products): See discussion for material 39B. Graphite epoxy and 23. Epiphen ER825A which apply here. Kevlar which is essentially a 1:1 mixture of these or structurally similar material should exhibit similar outgassing products that in terms of importance towards radiation darkening include phenols, phthalates, aromatic amines and to a lesser extent aromatic and aliphatic hydrocarbons.
- I. Radiation Sensitivity (Darkening): Moderate to high.

G. Degradation/Decomposition

(Kevlar)

2. Radiation

b. UV: Photodegradation of aromatic polyamides in the absence of $\rm O_2$ indicate CO as being the only volatile species. However, in air, carboxylic acid groups and $\rm CO_2$ dominate. (Refs. CAR78A, CAR78B).

IR spectra of aramid fibers in air show that yellowing probably results from products derived from $-C_6H_4$ -NH fragments, concentrations of carboxylic acid groups on the surface near the UV source or the formation of quinones (REFs. CAR78A, CAR78B, CAR86A).

Kevlar is extremely photo stable due to self screening or increased thickness.

- A. Material: 4 . Kapton Type H-Film
- B. Specification:
- C. System VCM (g): 2.252
- D. Use: Elec. insulation; Space: Outermost surface of spacecraft T-C blanket.
- E. Chemical Information: Polyimide.
 - 1. Structure

Pyromellitimide Film.

- 2. Curing Agent/Hardener/Catalysts: Aromatic diamine (possibly oxydianiline)
- 3. Additives: Polar solvent.

- 5-.

- 4. Fillers:
- F. Outgassing (Species Characterization):
 - GC/MS: Show migration on film due hostile ions (alkali metal, etc.), Cl⁻, K⁺, Na⁺ are most critical.
 - 2. IR
 - 3. UV:
- 4. HPLC/G.P.C.
- G. Degradation/Decomposition: H₂O Sensitive.
 - 1. Thermal/Aging: Although little chemical information is available, weight and property measurements indicate that at high temperatures this material is extremely stable to thermal aging (Ref. SRO 65A).
 - 2. Radiation Polymers of this type (polybenzimidizole) are among the most radiation resistant polymers known. Low dose rate electron irradiation produces rupture of the aromatic ether linkage in the molecule (REF FER 81A).
 - a. Ionizing
 - b. uv
 - c. VUV
- H. Summary (Most Probable Outgassing Products):

The thermal and radiation aging results given above suggest this material will outgas monomer, dimer and other low molecular weight olegomers on aging, but at very slow rates. While the latter appears favorable from a contamination point of view, it must be remembered that these materials, even before irradiation, typically absorb strongly in the uv and even into the visible regions of the solar spectrum, and darken even more with irradiation. The high system VCM for Kapton belies the inherent stability of this polymer. If the VCM is due to solvent outgassing, the typical solvents used in preparation of the material pose low to moderate darkening concerns; if, however, the system VCM is due to monomer outgassing, moderate to high concerns exist. This point should be checked.

I. Radiation Sensitivity (Darkening): Low to high.

- A. Material: 5A. Graphite Epoxy (Narmco T300/5208)
- B. Specification:
- C. System VCM (g): 1.514
- D. Use: Structural applications
- E. Chemical Information:
 - 1. Structure

Tetraglycidylmethylene dianiline (TGMDA). Typically used with aliphatic ketones or phenol-derived diluents.

- 2. Curing Agent/Hardener/Catalysts: Diaminodiphenylsulfone (DDS)
- 3. Additives
- 4. Fillers: T300 PAN Fibers containing 1% DEGBA by fibers Wt. (Un. Carbide)
- F. Outgassing (Species Characterization):
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:

- %-

- 1. Thermal/Aging: H_2O and CO_2 and, above $200^{O}C$, aliphatic ethers and alcohols, acetone, xylenes, benzene, toulene, phenol and substituted phenols (LUM81A, LUM82A, END86A).
- 2. Radiation
 - a. Ionizing Similar products to thermal aging with the addition of low molecular weight aliphatic hydrocarbons, olefins and aldehydes. Considerably higher number of specifies observed. (END86A)
 - b. UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products):
 Relative to potential darkening outgassing products, key materials of interest are the phenolic products and, to a lesser extent, the aromatic hydrocarbons and aliphatic hydrocarbons, olefins and carbonyl compounds. Although thermal/radiation studies gave no evidence for aminophenylsulfone derivatives or amines, which are present in the base material, studies on epoxies mechanically degraded (drilled under liquid nitrogen) did yield evidence for these species (ref. KOW82A).
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 5B. Graphite Epoxy (Hercules AS/3501)
- B. Specification: ___
- C. System VCM (g): 1.514
- D. Use: Structural
- E. Chemical Information:
 - Structure
 Tetraglycidylmethylene dianiline (TGMDA). Typically used with aliphatic
 ketones or phenol derived diluents.
 - 2. Curing Agent/Hardener/Catalysts: Diaminodiphenylsulfone (DDS)
 - 3. Additives: Celanese SU-8 epoxy NOVOLAC
 - 4. Fillers: T300 PAN fibers containing 1% DGEBA by fiber wt. (Un. Carbide.)
- F. Outgassing (Species Characterization):
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - 1. Thermal/Aging: $\rm H_2O$ and $\rm CO_2$ and, above $200^{\rm O}$ C, aliphatic ethers and alcohols, acetone, xylenes, benzene, toulene, phenol and substituted phenols (LUM81A, LUM82A, END86A).
 - 2. Radiation
 - a. Ionizing Similar products to thermal aging with the addition of low molecular weight aliphatic hydrocarbons, olefins and aldehydes. Considerably higher number of specifies observed. (END86A)
 - **b.** UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products):
 Relative to potential darkening outgassing products, key materials of interest are the phenolic products and, to a lesser extent, the aromatic hydrocarbons and aliphatic hydrocarbons, olefins and carbonyl compounds. Although thermal/radiation studies gave no evidence for aminophenylsulfone derivatives or amines, which are present in the base material, studies on epoxies mechanically degraded (drilled under liquid nitrogen) did yield evidence for these species (ref. KOW82A).
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 5C. Graphite Epoxy (Fiberite T300/934)
- B. Specification:
- C. System VCM (g): 1.514
- D. Use: Structural applications
- E. Chemical Information:
 - 1. Structure

Tetraglycidylmethylene dianiline (TGMDA)

2. Curing Agent/Hardener/Catalysts: Diaminodiphenylsulfone (DDS), BF $_3$ NH $_2$ C $_2$ H $_5$ or BF $_3$ NHC $_5$ H $_1$ O.

- 3. Additives: Epoxy novolac, SU-8, Celanese
- 4. Fillers: T300 polyacrylonitrile (PAN Fibers) containing 1% DEBPA by fiber wt. (Un. Carbide).
- F. Outgassing (Species Characterization): H₂0
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:

- 5-

- 1. Thermal/Aging: $\rm H_2O$ and $\rm CO_2$ and, above $200^{\rm O}$ C, aliphatic ethers and alcohols, acetone, xylenes, benzene, toulene, phenol and substituted phenols (LUM81A, LUM82A, END86A).
- 2. Radiation
 - a. Ionizing Similar products to thermal aging with the addition of low molecular weight aliphatic hydrocarbons, olefins and aldehydes. Considerably higher number of specifies observed. (END86A)
 - b. UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products):
 Relative to potential darkening outgassing products, key materials of interest
 are the phenolic products and, to a lesser extent, the aromatic hydrocarbons and
 aliphatic hydrocarbons, olefins and carbonyl compounds. Although thermal/radiation
 studies gave no evidence for aminophenylsulfone derivatives or amines, which are
 present in the base material, studies on epoxies mechanically degraded (drilled
 under liquid nitrogen) did yield evidence for these species (ref. KOW82A).
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 6. PIM-984 Epoxy B. Specification: System VCM (g): 1.221 D. Use: Chemical Information: 1. Structure: Diglycidylether of Bisphenol-A (DGEBA) Curing Agent/Hardener/Catalysts: 4% piperidine, 6% 2-ethyl-4(-5)methylimidazole. 3. Additives: 4. Fillers: Cabosil (sodium silicate). F. Outgassing (Species Characterization): 1. GC/MS IR: Shows the presence of carbonyl absorptions occurring during 2. polymerization leading to ketone formation (1,1,1 trichloroacetane, ketone carbonyls). 3. UV HPLC/G.P.C.: Shows the presence of unreacted diglycidylether. Degradation/Decomposition: 1. Thermal/Aging 2. Radiation Ionizing a. b. UV VUV
- I. Radiation Sensitivity (Darkening): Moderate to high.

See attached sheet for summary.

H. Summary (Most Probable Outgassing Products):

50. PIM-984 Epoxy (Cont.)

H. Summary (Most Probable Outgassing Products):

Relative to potential darkening outgassing products, key materials of interest are the phenolic products and, to a lesser extent, the aromatic hydrocarbons and aliphatic hydrocarbons, olefins and carbonyl compounds. Although thermal/radiatio studies gave no evidence for aminophenylsulfone derivatives or amines, which are present in the base material, studies on epoxies mechanically degraded (drilled under liquid nitrogen) did yield evidence for these species (Ref. KOW82A).

Although some heterocyclic amine curing agents (piperidene and imidazoles) could survive the curing process and later outgas, these should present minimal problems with regard to radiation induced darkening.

E.	Che	mical Information: Polyester fiber/thermoset rubber/R. Structure
	2.	Curing Agent/Hardener/Catalysts:
	3.	Additives:
	4.	Fillers:
F.	0ut 1.	gassing (Species Characterization): GC/MS
	2.	IR
	3.	UV
	4.	HPLC/G.P.C.
G.	Deg:	radation/Decomposition: Thermal/Aging
	2.	Radiation a. Ionizing
		b. UV
		c. VUV
H.	Sum	mary (Most Probable Outgassing Products):
I.	Radi	Lation Sensitivity (Darkening):

A-16

A. Material: 7. 3M Tape X-1157

Product discontinued/3M

B. Specification:

D. Use: Tape

C. System VCM (g): 0.950

- A. Material: 8. RTV 566
- B. Specification:
- C. System VCM (g): 0.862
- D. Use:
- E. Chemical Information:
 - 1. Structure: Methyl phenyl silicone
 - 2. Curing Agent/Hardener/Catalysts: Dibutyl tin laurate
 - 3. Additives:
 - 4. Fillers:
- F. Outgassing (Species Characterization):
 - GC/MS: Spectra of this and like materials generally indicate that low molecular weight monomers, dimers, etc., are the chief outgassing components (Ref. COL 76A).
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - 1. Thermal/Aging: Thermal decomposition and pyrolysis studies of silicones generally indicate monomeric or low molecular weight polymeric groups of the parent silicone are the chief volatile products (KLE80A, LUC82A).
 - 2. Radiation
 - a. Ionizing
 - ъ. uv
 - c. VUV
- H. Summary (Most Probable Outgassing Products):

Data cited above indicate the most likely outgassing products are low molecular weight methyl phenyl silicones. Indeed both methyl and methyl phenyl have been noted to be outgassers in spacecraft environments (COL79A, COL79B). This coupled with the data indicating that, although methyl phenyl silicones are more stable to particulate radiation than are the methyl silicones, they are more sensitive to discoloration, to vacuum uv irradiation (Refs. FLE73A, GI077A). uv irradiation (Refs. FLE73A, GI077A) indicates methyl phenyl silicones are of primary concern.

 Radiation Sensitivity (Darkening): Moderate.

- A. Material: 9. Epoxy Fiberglass; Micaply EG18T/802T
- B. Specification:

Also: MIL-P-13949

- C. System VCM (g): 0.618
- D. Use: Printed wiring boards (laminant).
- E. Chemical Information:
 - 1. Structure: Diglycidylether of Bisphenol-A, DGEBA (advanced liquid to form Tetrabromobisphenol A.
 - 2. Curing Agent/Hardener/Catalysts: Dicyandiamide (DICY)
 - 3. Additives: FR-4 flame retardant; chrome, organic titanate or silane on the surface.
 - 4. Fillers: Copper cladding; glass cloth (Type E) as reinforcing material. Solvents, acetone, methyl ethyl ketone.
- F. Outgassing (Species Characterization):
 - 1. GC/MS: Principally $\rm H_2O$, $\rm CO_2$, $\rm CO$ at 25 150°C (Refs. BR067A, VAS78A, SAN85A).
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.: Low molecular weight phenols from HPLC of Bisphenol-A (Ref. SAN85A).
- G. Degradation/Decomposition:
 - Thermal/Aging: Volatile products included H₂O, CO, CH₃OCH₃, CH₂= CHCH₂OH, CH₂CHCHO, CH₂=CH₂, CH₃CH=CH₂, phenol, substituted phenols, aromatic esters with carbonyls and or ethylenic groups (280°C), (Refs. GRA85A, GRA85B, GRA86A).
 - 2. Radiation
 - a. Ionizing: UV and IR studies of electron irradiated material gave results consistent with thermal/aging studies. Carbonyl and ethylenic bonds were formed, as well as aromatic free radicals (Refs. BUR80A, BUR82A).
 - b. UV: Similar to thermal/aging with addition of $\rm H_2$ and aromatic hydrocarbons (Refs. GRA85C, GRA86B).
 - c. VUV
- H. Summary (Most Probable Outgassing Products): Outgassing products of principle concern with regard to potential radiation darkening are the phenols and substituted aromatic esters and to a lesser extent the carbonyl containing species and unsaturated hydrocarbons.
- I. Radiation Sensitivity (Darkening): Moderate to high.

Material: 10. Polyimide PWB В. Specification: MIL-P-13949/10 System VCM (g): 0.572 D. Use: Printed wiring boards. E. Chemical Information: Polyimide (Kerimid 601) 1. Structure Bis-maleimide. 2. Curing Agent/Hardener/Catalysts: Methylene dianiline. 3. Additives: Solvent for resin varnish -N-Methyl-2 Pyrrolidone (NMP). 4. Fillers: Cu cladding, glass fabric base (B-stage). Outgassing (Species Characterization): 1. GC/MS 2. IR 3. UV 4. HPLC/G.P.C. G. Degradation/Decomposition: 1. Thermal/Aging 2. Radiation: No indication of deterioration in phys. or elec. prop(s). Ionizing: Up to a dose of 1.5X108 rads. radiation resistance.

Summary (Most Probable Outgassing Products):

UV

c. VUV

ъ.

- A. Material: 11. Stephan Foam G504
- B. Specification:
- C. System VCM (g): 0.444
- D. Use: Structural panels, potting, buoyancy.
- E. Chemical Information: Polyurethane foam.
 - 1. Structure
 - a. Toulene-2,4 Diisocyanate (TDI).
 - b. Polyol resin.

Mixing ratio (by weight): 64 parts a + 33 parts b.

- 2. Curing Agent/Hardener/Catalysts: Water blown system, amine catalyst.
- 3. Additives:
- 4. Fillers:
- F. Outgassing (Species Characterization):
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - Thermal/Aging: Thermal aging at 250 360°C indicate primary products were N₂, CO and CO₂ (probably resulting from decomposition of NCO groups) as well as phthalates, aromatic amines, phenols and aromatic hydrocarbons (Refs. FOT83A, KAL86A, FOT81A, EID80A, ERI80A, LEV80A).
 - 2. Radiation
 - a. Ionizing
 - b. uv
 - c. VUV
- H. Summary (Most Probable Outgassing Products): Phthalates, aromatic amines, phenols and, to a lesser extent, aromatic hydrocarbons.
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 12. EC3924 Primer
- B. Specification:
- C. System VCM (g): 0.416
- D. Use: Paint primer.
- E. Chemical Information: Polyurethane.
 - 1. Structure
 - 2. Curing Agent/Hardener/Catalysts: Alkaline amines.
 - 3. Additives: Aminohydrogen functional polyamide polyisocyanate, polyol topcoat.
 - 4. Fillers: Strontium chromate, TiO2 pigment, Si extenders.
- F. Outgassing (Species Characterization):
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - 1. Thermal/Aging: Thermal aging at 250 360° C indicate primary products were N_2 , CO and CO_2 (probably resulting from decomposition of NCO groups) as well as phthalates, aromatic amines, phenols and aromatic hydrocarbons (Refs. FOT83A, KAL86A, FOT81A, EID80A, ERI80A, LEV80A, GLA84A).
 - 2. Radiation
 - a. Ionizing
 - b. UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products):
 Phthalates, aromatic amines, phenols and, to a lesser extent, aromatic hydrocarbons.
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 13. Uralane 5753 A/B (LV)
- B. Specification:

See also: MIL-I-46058C.

- C. System VCM (g): 0.332
- D. Use: Casting comp. for elec./electron. small modules and complicated circuitry.
- E. Chemical Information:
 - 1. Structure
- a. Org. isocyanate.

b. Hydroxytermin polyols (100%).

Isocyanate termin. adducts.

4,4' Diphenylmethane Diisocyanate

(~80%).

High mw polym(s) MDI (~20%).

Get crystall. MDI below 16°C - MDI dimer above 50°C.

- . 2. Curing Agent/Hardener/Catalysts: Antifoam agent (AF.4).
 - 3. Additives
 - 4. Fillers
- F. Outgassing (Species Characterization):
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - 1. Thermal/Aging: Thermal aging at 250 360° C indicate primary products were N₂, CO and CO₂ (probably resulting from decomposition of NCO groups) as well as phthalates, aromatic amines, phenols and aromatic hydrocarbons (Refs. FOT83A, KAL86A, FOT81A, EID80A, ERI80A, LEV80A).
 - 2. Radiation
 - a. Ionizing
 - b. UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products): Phthalates, aromatic amines, phenols and, to a lesser extent, aromatic hydrocarbons.
- I. Radiation Sensitivity (Darkening): Moderate to high.

A.	Material: 14. Epoxy Adhesive
В.	Specification:
c.	System VCM (g): 0.318
D.	Use: Electrical and Aerospace Adhesives.
E.	Chemical Information: 1. Structure: Diglycidylether of Bisphenol-A, DGEBA (Epon 828/V140, Shell Chemcical Co.)
	Mixing Ratio: 100 pts. Epon 828 21 pts. Versamid-140 13 pts. Methane Diamine
	2. Curing Agent/Hardener/Catalysts: Polyamide (V-140); Methane Diamine.
	3. Additives:
	4. Fillers:
F.	Outgassing (Species Characterization): 1. GC/MS
	2. IR
	3. UV
	4. HPLC/G.P.C.
G.	Degradation/Decomposition: 1. Thermal/Aging
	2. Radiation a. Ionizing
	Ъ. UV
	c. VUV
н.	Summary (Most Probable Outgassing Products):
I.	Radiation Sensitivity (Darkening):

- A. Material: 15. Uralane 5750 A/B (LV)
- B. Specification:
- C. System VCM (g): 0.265
- D. Use: Printed circuit boards, elec./electron. components.
- E. Chemical Information: Polyurethane.
 - 1. Structure
- a. 4,4' Diphenylmethane Diisocyanate.
 (MDI) + high mw polym(s) 90%.
 Toulene <10%.
 Solid yellow.
 - b. Hydroxy termin. polyols >80%.
 Toulene <10%.
 MEK < 10%.
 Fluorescent Dye <1%.
 Hazy Amber.

Mix ratio: 1 - 18 pts a + 100 pts b + 20 pts 5750 thinner.

- 2. Curing Agent/Hardener/Catalysts:
- 3. Additives:
- 4. Fillers:
- F. Outgassing (Species Characterization):
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - 1. Thermal/Aging: Thermal aging at 250 360° C indicate primary products were N₂, CO and CO₂ (probably resulting from decomposition of NCO groups) as well as phthalates, aromatic amines, phenols and aromatic hydrocarbons (Refs. FOT83A, KAL86A, FOT81A, EID80A, ER180A, LEV80A).
 - 2. Radiation
 - a. Ionizing
 - b. UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products): Phthalates, aromatic amines, phenols and, to a lesser extent, aromatic hydrocarbons.
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 16. Silicone
- B. Specification: MIL-ZZR-765
- C. System VCM (g): 0.230
- D. Use: Dampening and gasketing
- E. Chemical Information: Rubber, silicone1. Structure: Methyl phenyl silicone
 - 2. Curing Agent/Hardener/Catalysts:
 - 3. Additives:
 - 4. Fillers:
- F. Outgassing (Species Characterization):
 - 1. GC/MS: Spectra of this and like materials generally indicate that low molecular weight monomers, dimers, etc., are the chief out gassing components (Ref. COL 76A).
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - 1. Thermal/Aging: Thermal decomposition and pyrolysis studies of silicones generally indicate monomeric or low molecular weight polymeric groups of the parent silicone are the chief volatile products (KLE80A, LUC82A).
 - 2. Radiation
 - a. Ionizing
 - b. UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products): Data cited above indicate the most likely outgassing products are low molecular weight methyl phenyl silicone. Indeed both methyl and methyl phenyl have been noted to be outgassers in spacecraft environments (COL79A, COL79B). This coupled with the data indicating that, although methyl phenyl silicones are more stable to particulate radiation than are the methyl silicones, they are more sensitive to discoloration, to vacuum uv irradiation (Refs. FLE73A, GIO77A).
- I. Radiation Sensitivity (Darkening): Moderate

- A. Material: 17. Epoxy Prepreg Also: MIL-P-13949E; Micaply: 102-68 (B-stage), no flow.
- B. Specification:
- C. System VCM (g): 0.217
- D. Use: Laminant (fiberglass reinforced) for printed circuit boards.
- E. Chemical Information:
 - 1. Structure: Diglycidylether of Bisphenol-A, DGEBA (advanced liquid to form Tetrabromobisphenol-A).
 - 2. Curing Agent/Hardener/Catalysts: Most probably DICY or DDS.
 - 3. Additives: FR-4 flame retardant, solid copper sheeting, glass cloth as reinforcing material.
 - 4. Fillers/solvents: Acetone methyl ethyl ketone, 2-methoxyethanol, dimethyl-formanide.
- F. Outgassing (Species Characterization):
 - 1. GC/MS: Principally $\rm H_2O$, $\rm CO_2$, $\rm CO$ at 25-150 $^{\rm O}$ C (Refs. BRO67A, VAS78A, SAN85A).
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.: Low molecular weight phenols from HPLC of Bisphenol-A (Ref. SAN85A).
- G. Degradation/Decomposition:
 - Thermal/Aging: Volatile products included H₂O, CO, CH₃OCH₃, CH₂= CHCH₂OH, CH₂CHCHO, CH₂=CH₂, CH₃CH=CH₂, phenol, substituted phenols, aromatic esters with carbonyls and or ethylenic groups (280°C), (Refs. GRA85A, GRA85B, GRA86A).
 - 2. Radiation
 - a. Ionizing: UV and IR studies of electron irradiated material gave results consistent with thermal/aging studies. Carbonyl and ethylenic bonds were formed, as well as aromatic free radicals (Refs. BUR80A, BUR82A).
 - b. UV: Similar to thermal/aging with addition of ${\rm H_2}$ and aromatic hydrocarbons (Refs. GRA85C, GRA86B).
 - c. VUV
- H. Summary (Most Probable Outgassing Products): Outgassing products of principle concern with regard to potential radiation darkening are the phenols and substituted aromatic esters and to a lesser extent the carbonyl containing species and unsaturated hydrocarbons.
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 18. Epiphen ER 825-A
- B. Specification:

Also: Fed. Specif. MMM-A-134, TyI

- C. System VCM (g): 0.209
- D. Use: Adhesive, epoxy resin, metal to metal structural bonding.
- E. Chemical Information: 4 part liquid epoxidized Novolac resin system.
 - 1. Structure

Epiphen 825-A resin.

- Curing Agent/Hardener/Catalysts: Modifier "T" polythiol.
- 3. Additives: Converter polyfunctional amine (dialkylamine and dialkylenetriamine) alkylalkanolamine family.
- 4. Fillers: Mica powder.
- F. Outgassing (Species Characterization):
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - 1. Thermal/Aging: H_2O and CO_2 and, above $200^{O}C$, aliphatic ethers and alcohols, acetone, xylenes, benzene, toulene, phenol and substituted phenols (LUM81A, LUM82A, END86A).
 - 2. Radiation
 - a. Ionizing Similar products to thermal aging with the addition of low molecular weight aliphatic hydrocarbons, olefins and aldehydes. Considerably higher number of specifies observed. (END86A)
 - b. UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products): Relative to potential darkening outgassing products, key materials of interest are the phenolic products and, to a lesser extent, the aromatic hydrocarbons and aliphatic hydrocarbons, olefins and carbonyl compounds. Although thermal/radiation studies gave no evidence for aminophenylsulfone derivatives or amines, which are present in the base material, studies on epoxies mechanically

degraded (drilled under liquid nitrogen) did yield evidence for these species (ref. KOW82A).

I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 19. FM 123-2
- B. Specification:

Also: Federal Specification: MMM-A-132 Tyl Cl₂
Military Specification: MIL-A-25463B

- C. System VCM (g): 0.198
- D. Use: Structural bonding, metal to metal; metal honeycomb sandwich.
- E. Chemical Information: Modified Nitrile epoxy adhesive
 - 1. Structure: 2-part system:
 - A. Digylcidyl ether of Bisphenol-A (DGEBA)
 - B. Carboxylated nitrile (65% butadiene, 35% acrylonitrile, 5% acrylic acid)
 - 2. Curing Agent/Hardener/Catalysts: Dicyandiamide (non-resinone hardener BR-127 corrosion inhibiting primer.
 - 3. Additives: Chromium oxide, 3-(p-chlorophenyl)1, 1-dimethyl uren (Monuron, herbicide), uv stabilizing absorbant.
 - 4. Fillers: Dacron polyester mat (Refs. PIT82A, MOR82A).
- F. Outgassing (Species Characterization): From 30 120°C outgassing products are: H₂O, butyl diglycidyl ether, Bisphenol-A, dicyandiamide, DGEBA, sec. amine, toulene amine (TIR81A).
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - 1. Thermal/Aging
 - 2. Radiation
 - a. Ionizing
 - b. UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products):
- I. Radiation Sensitivity (Darkening):

- A. Material: 20. Cotton Phenolic
- B. Specification:

Also: MIL-P-15035C

- C. System VCM (g): 0.187
- D. Use: Electrical insulation and mechanical
- E. Chemical Information: Epoxy phenolic resin (novolac)
 - 1. Structure
 - 2. Curing Agent/Hardener/Catalysts: Hexamethylenetetramine (polyfunctional amine).
 - Additives:
 - 4. Fillers: Cotton fabric base
- F. Outgassing (Species Characterization):
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - 1. Thermal/Aging: $\rm H_2O$ and $\rm CO_2$ and, above $200^{\rm O}$ C, aliphatic ethers and alcohols, acetone, xylenes, benzene, toulene, phenol and substituted phenols (LUM81A, LUM82A, END86A).
 - 2. Radiation
 - a. Ionizing Similar products to thermal aging with the addition of low molecular weight aliphatic hydrocarbons, olefins and aldehydes. Considerably higher number of specifies observed. (END86A)
 - b. UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products): Relative to potential darkening outgassing products, key materials of interest are the phenolic products and, to a lesser extent, the aromatic hydrocarbons and aliphatic hydrocarbons, olefins and carbonyl compounds. Although thermal/radiation studies gave no evidence for aminophenylsulfone derivatives or amines, which are present in the base material, studies on epoxies mechanically degraded (drilled under liquid nitrogen) did yield evidence for these species (ref. KOW82A).
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 21. Solithane 113 B. Specification: C. System VCM (g): 0.173 D. Use: E. Chemical Information: Polyurethane 1. Structure 2. Curing Agent/Hardener/Catalysts:
 - 3. Additives:
 - 4. Fillers:
 - F. Outgassing (Species Characterization):
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
 - G. Degradation/Decomposition:
 - 1. Thermal/Aging: Thermal aging at 250 360° indicate primary products were N_2 , CO and CO_2 (probably resulting from decomposition of NCO groups) as well as phthalates, aromatic amines, phenols and aromatic hydrocarbons (Refs. FOT83A, KAL86A, FOT81A, EID80A, ERI80A, LEV80A).
 - 2. Radiation
 - a. Ionizing
 - b. UV
 - c. VUV
- Summary (Most Probable Outgassing Products): aromatic amines, phenols and, to a lesser extent, aromatic Phthalates, hydrocarbons.
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 22. EC2216 (Scotchweld)
- B. Specification:
- C. System VCM (g): 0.171
- D. Use: Structural; bonding electrical parts; threaded fasteners
- E. Chemical Information: Modified epoxy
 - 1. Structure: 2-part system
 - A. Diglycidyl ether of Bisphenol-A (DGEBA)
 - B. Modified amine

Mixing Ratio: 5 parts A + 7 part B (by wt.)
2 parts A + 3 parts B (by vol)

- 2. Curing Agent/Hardener/Catalysts: Modified amine
- Additives:
- 4. Fillers:
- F. Outgassing (Species Characterization):
 - 1. GC/MS: Principally H_2O , CO_2 , CO_3 , at 25-150°C (Refs. BR067A, VAS78A, SAN85A).
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.: Low molecular weight phenols from HPLC of Bisphenol-A (Ref. SZA78A).
- G. Degradation/Decomposition:
 - Thermal/Aging: Volatile products included H₂O, CO, CH₃OCH₃, CH₂= CHCH₂OH, CH₂CHCHO, CH₂=CH₂, CH₃CH=CH₂, phenol, substituted phenols, aromatic esters with carbonyls and or ethylenic groups (280^oC), (Refs. GRA85A, GRA85B, GRA86A).
 - 2. Radiation
 - a. Ionizing: UV and IR studies of electron irradiated material gave results consistent with thermal/aging studies. Carbonyl and ethylenic bonds were formed, as well as aromatic free radicals (Refs. BUR80A, BUR82A).
 - b. UV: Similar to thermal/aging with addition of H_2 and aromatic hydrocarbons (Refs. GRA85C, GRA86B).
 - c. VUV
- H. Summary (Most Probable Outgassing Products): Outgassing products of principle concern with regard to potential radiation darkening are the phenols and substituted aromatic esters and to a lesser extent the carbonyl containing species and unsaturated hydrocarbons.
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 23. Ablefilm 546
- B. Specification:
- C. System VCM (g): 0.143
- D. Use: Thermally conductive adhesive film
- E. Chemical Information: Polyester
 - 1. Structure: Polyethylene Terephthalate
 - 2. Curing Agent/Hardener/Catalysts:
 - 3. Additives:
 - 4. Fillers/Solvents: Glass fabric; Cyclohexanone.
- F. Outgassing (Species Characterization):
 - GC/MS: Phthalates, in particular, di-2-ethylhexyl phthalate (COL72A, COL76A, COL79B)
 - 2. IR: Extraction of polymer in organic solvents indicated presence of cyclic trimer as well as other oligomers (ADA82A).
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - 1. Thermal/Aging: Main Chain scission of the ester links, accompanied by decarboxylation and formation of CO, CO₂, acetaldehyde, aromatic acids and vinyl esters (BED81A, ADA82A, ING82A, SUE84A, OHT86A).
 - 2. Radiation
 - a. Ionizing: Chain scission and crosslinking indicative of main chain rupture (HAN69A, BEL83A).
 - b. UV: Photochemical yields of CO (and CO₂) as well as COOH end groups indicate main chain scission as the dominant process (DAY71A, WIL73A, ILI85A).
 - c. VUV: Yields of CO and ${\rm CO}_2$, and decrease in the oxygen to carbon ratio suggest that main chain scission with decarboxylation is major degradation made (LAZ86A).
- H. Summary (Most Probable Outgassing Products): All of the above evidence points to monomers, dimers, trimers and other low molecular weight oligomers as the chief expected outgassing products. Thus low molecular weight phthalates, which are among the most common outgassing products found in spacecraft sampling (COL79B) are the most likely species of concern with regard to potential radiation induced darkening. Indeed, at low temperatures, highly colored, stabilized ionic species have been observed (TOR85A).
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 24. Velcro-100-Polyester
- B. Specification: MIL-F-21840 TyII C13
- C. System VCM (g): 0.127
- D. Use: Fastener tapes, hook and pile, synthetic (8.0 mil polyester hook; polyester ground; tapes all polyester.
- E. Chemical Information:
 - 1. Structure: Polyester (Polyethylene Terephthalate, PET). PET is prepared commercially by two routes, ester interchange (EI) and direct esterification (Ref. TES85A).
 - 2. Curing Agent/Hardener/Catalysts: Mn (OAC) $_2$ and Sb $_2$ O $_3$ are used as catalyst with EI. Sb $_2$ O $_3$ only is used for direct esterification.
 - 3. Additives: Color agents: green 3422 and white 3056; coated with polymeric or elastomeric undercoat.
 - 4. Fillers: glass fibers for stability (?); talc and particulates.
- F. Outgassing (Species Characterization): PET is susceptible to actinic degradation owing to chromophores in the repeating unit.
 - 1. GC/MS: Show CO and CO₂ to be the only significant voltatile degradation products (WIL73A).
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - 1. Thermal/Aging: GC, GC/MS, IR, specific ion electrode, H.P.L.C., wet chemistry and colorimetric (drager tubes) analyses show PET to be decomposed into sixty-eight (68) different species (LEV86A). Pyrolysis M5 and CP/MAS ¹³C-NMR and FTIR show that after thermal clevage of PET, free carboxyl and vinyl ester groups are formed by two competing reaction pathways. Low molecular weight fragments enter into the vapor phase and undergo further degradation primarily to CO₂, CO, and acetaldehyde. (SUE84A, BED81A). Other thermal decomposition products of interest are divinyl terephthalate, methyl-1-hydroxyethyl terephthalate, styene, vinyl compounds and methane.
 - 2. Radiation
 - a. Ionizing: y-irradiated PET investigated by esr and optical absorption measurements (CO^{60} at dose rate of 3.8 X 10^5 rad/h, in the dark at -196°C) show that PET films develop a reddish purple color and show an esr spectra assigned to ionic species of PET as compared to model compounds (Ref. TOR85A). There is very little degradation of PET at low dosage due to aromaticity from benzene ring structures which can protect polyesters from the degrading effects of radiation (BEL83A).
 - b. UV: Photo-degradation of PET (film) show that the main chromophore (240 320 nm) is the -0-CO-C₆H₄-CO-O-group (Refs. ILI85A, WIL73A). UV causes an increase in the quantity of carboxylic acid end groups with the formation of radicals and volatile products. The dielectric loss factors increases so rapidly that the total electrical conductivity loss factor increases and the electrical conductivity also increases causing the insulation properties of PET to deteriorate during irradiation.
 - c. VUV
- H. Summary (Most Probable Outgassing Products):
- I. Radiation Sensitivity (Darkening):

- A. Material: 26 Dacron Tape
- B. Specification: MIL-T-43435B, TyI
- C. System VCM (g): 0.111
- D. Use: Tape, Lacing and tying (flat braided).
- E. Chemical Information: Polyester (Dacron)/polyamide (nylon)
 - 1. Structure: Poly (ethylene terephthalate)-E-caprolactone CO-polymer; continuous filament yarn).
 - 2. Curing Agent/Hardener/Catalysts:
 - 3. Additives:
 - 4. Fillers:
- F. Outgassing (Species Characterization):
 - GC/MS: Phthalates, in particular, di-2-ethylhexyl phthalate (COL72A, COL76A, COL79B)
 - 2. IR: Extraction of polymer in organic solvents indicated presence of cyclic trimer as well as other oligomers (ADA82A).
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - 1. Thermal/Aging: Main Chain scission of the ester links, accompanied by decarboxylation and formation of CO, CO₂, acetaldehyde, aromatic acids and vinyl esters (BED81A, ADA82A, ING82A, SUE84A, OHT86A).
 - 2. Radiation
 - a. Ionizing: Chain scission and crosslinking indicative of main chain rupture (HAN69A, BEL83A).
 - b. UV: Photochemical yields of CO (and CO₂) as well as COOH end groups indicate main chain scission as the dominant process (DAY71A, WIL73A, ILI85A).
 - c. VUV: Yields of CO and ${\rm CO}_2$, and decrease in the oxygen to carbon ratio suggest that main chain scission with decarboxylation is major degradation made (LAZ86A).
- H. Summary (Most Probable Outgassing Products): All of the above evidence points to monomers, dimers, trimers and other low molecular weight oligomers as the chief expected outgassing products. Thus low molecular weight phthalates, which are among the most common outgassing products found in spacecraft sampling (COL79B) are the most likely species of concern with regard to potential radiation induced darkening. Indeed, at low temperatures, highly colored, stabilized ionic species have been observed (TOR85A).
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 28. Stathane 823
- B. Specification:
- C. System VCM (g): 0.084
- D. Use: Structural applications
- E. Chemical Information: Rigid Polyurethane Foam
 - 1. Structure: 2-part system:
 - A. Toulene Diisocyanate B. Polyether Polyol Benzoyl Chloride

B. Polyether/polyester blend

Mixing Ratio: 100 parts A + 2 parts B (by weight)

- 2. Curing Agent/Hardener/Catalysts: Tertiary Amine (probably tin salts, synergistic effect).
- 3. Additives: CO2 blown
- 4. Fillers:
- Outgassing (Species Characterization):
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - 1. Thermal/Aging: Thermal aging at $250 360^{\circ}$ indicate primary products were N_2 , CO and CO_2 (probably resulting from decomposition of NCO groups) as well as phthalates, aromatic amines, phenols and aromatic hydrocarbons (Refs. FOT83A, KAL86A, FOT81A, EID80A, ERI80A, LEV80A).
 - 2. Radiation
 - a. Ionizing
 - **b.** UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products): Phthalates, aromatic amines, phenols and, to a lesser extent, aromatic hydrocarbons.
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 29. Chemglaze Z302
- B. Specification:
- C. System VCM (g): 0.054
- D. Use: Paint (glossy black)
- E. Chemical Information: Polyurethane binder
 - 1. Structure
 - 2. Curing Agent/Hardener/Catalysts:
 - 3. Additives: Carbon
 - 4. Fillers:
- F. Outgassing (Species Characterization):
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:

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- 1. Thermal/Aging: Thermal aging at 250 360° C indicate primary products were N₂, CO and CO₂ (probably resulting from decomposition of NCO groups) as well as phthalates, aromatic amines, phenols and aromatic hydrocarbons (Refs. FOT83A, KAL86A, FOT81A, EID80A, ER180A, LEV80A).
- 2. Radiation
 - a. Ionizing
 - **b. UV**
 - c. VUV
- H. Summary (Most Probable Outgassing Products): Phthalates, aromatic amines, phenols and, to a lesser extent, aromatic hydrocarbons.
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 30. Diallylphthalate
- B. Specification: MIL-M-14G TySDG-F
- C. System VCM (g): 0.044
- D. Use: Molding and Coatings for electronic devices; electrical insulation
- E. Chemical Information: Diallylphthalate resid (DAP)
 - 1. Structure
 - 2. Curing Agent/Hardener/Catalysts: Hydrogen peroxide (H_2O_2) or a combination of H_2O_2 and an organic peroxide (dibenzoyl peroxide).
 - 3. Additives: Hydroquinone, antimony oxide (flame retardant, calcium sterate, DAP monomer, DAP prepolymer).
 - 4. Fillers/Solvents: Short glass fibers, glass spheres (<325 mesh), viny1 silone (coating glass fibers); acetone (Refs. BAK82A).
- F. Outgassing (Species Characterization):
 - 1. GC/MS: Phthalates, in particular, di-2-ethylhexyl phthalate (COL72A, COL76A, COL79B).
 - 2. IR: Extraction of polymer in organic solvents indicated presence of cyclic trimer as well as other oligomers (ADA82A).
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - Thermal/Aging: Main chain scission of the ester links, accompanied by decarboxylation and formation of CO, CO₂, acetaldehyde, aromatic acids and vinyl esters (BED81A, ADA82A, ING82A, SUE84A, OTH86A).
 - 2. Radiation
 - a. Ionizing: Chain scission and crosslinking indicative of main chain rupture (HAN69A, BEL83A).
 - b. UV: Photochemical yields of CO (and ${\rm CO_2}$) as well as COOH end groups indicate main chain scission as the dominant process (DAY71A, WIL73A, ILI85A).
 - c. VUV: Yields of CO and ${\rm CO}_2$, and decrease in the oxygen to carbon ratio suggest that main chain scission with decarboxylation is major degradation made (LAZ86A).
- H. Summary (Most Probable Outgassing Products):
 - All of the above evidence points to monomers, dimers, trimers and other low molecular weight oligomers as the chief expected outgassing products. Thus low molecular weight phthalates, which are among the most common outgassing products found in spacecraft sampling (COL79B) are the most likely species of concern with regard to potential radiation induced darkening. Indeed, at low temperatures, highly colored, stabilized ionic species have been observed (TOR85A). The comments above on outgassing and degradation apply specifically to polyethylene terephthalate; however, they should also be indicative of terephthalate degradation and outgassing in general.
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 33. Kynar Sleeving
- B. Specification: MIL-I-23053/8
- C. System VCM (g): 0.040
- D. Use: Electrical insulation sleeving, heat shrinkable
- E. Chemical Information: Polyvinylidine fluoride
 - 1. Structure

Polymer of : 1,1-difluoroethylene-vinylidine fluoride commercially preferred monomer precursor: 1,1-difluoroethane, vinylidine fluoride and 1,1,1, Trichloroethane.

- 2. Curing Agent/Hardener/Catalysts:
- 3. Additives:
- 4. Fillers:
- F. Outgassing (Species Characterization):
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - 1. Thermal/Aging
 - 2. Radiation
 - a. Ionizing
 - b. UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products):
- I. Radiation Sensitivity (Darkening):

- A. Material: 34. Scotchcast 281
- B. Specification:
- C. System VCM (g): 0.035
- D. Use: Impregnation and encapsulation of electronic components
- E. Chemical Information: Epoxy liquid resin (2-part system)
 - 1. Structure

Mixing Ratio:

A:B (2:3 by wt.)

(37:63 vol %)

- 2. Curing Agent/Hardener/Catalysts:
- 3. Additives:
- 4. Fillers:
- F. Outgassing (Species Characterization):
 - 1. GC/MS: Principally H_2O , CO_2 , CO_3 , at 25-150°C (Refs. BR067A, VAS78A, SAN85A).
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.: Low molecular weight phenols from HPLC of Bisphenol-A (Ref. SZA78A).
- G. Degradation/Decomposition:

- 5-

- Thermal/Aging: Volatile products included H₂O, CO, CH₃OCH₃, CH₂= CHCH₂OH, CH₂CHCHO, CH₂=CH₂, CH₃CH=CH₂, phenol, substituted phenols, aromatic esters with carbonyls and or ethylenic groups (280°C), (Refs. GRA85A, GRA85B, GRA86A).
- 2. Radiation
 - a. Ionizing: UV and IR studies of electron irradiated material gave results consistent with thermal/aging studies. Carbonyl and ethylenic bonds were formed, as well as aromatic free radicals (Refs. BUR80A, BUR82A).
 - b. UV: Similar to thermal/aging with addition of ${\rm H_2}$ and aromatic hydrocarbons (Refs. GRA85C, GRA86B).
 - c. VUV
- H. Summary (Most Probable Outgassing Products): Outgassing products of principle concern with regard to potential radiation darkening are the phenols and substituted aromatic esters and to a lesser extent the carbonyl containing species and unsaturated hydrocarbons.
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 35. Chemglaze A276
- B. Specification:
- C. System VCM (g):
- D. Use: Paint (flat white)
- E. Chemical Information:
 - 1. Structure
 - 2. Curing Agent/Hardener/Catalysts:
 - 3. Additives: Flattening agent; Titanium dioxide.
 - 4. Fillers:
- F. Outgassing (Species Characterization):
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - 1. Thermal/Aging: Thermal aging at 250 360° C indicate primary products were N₂, CO and CO₂ (probably resulting from decomposition of NCO groups) as well as phthalates, aromatic amines, phenols and aromatic hydrocarbons (Refs. FOT83A, KAL86A, FOT81A, EID80A, ER180A, LEV80A).
 - 2. Radiation
 - a. Ionizing
 - b. UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products): Phthalates, aromatic amines, phenols and, to a lesser extent, aromatic hydrocarbons.
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 35B. Chemglaze A276
- B. Specification:
- C. System VCM (g): 0.031
- D. Use: Paint
- E. Chemical Information: Polyurethane binder
 - 1. Structure
 - 2. Curing Agent/Hardener/Catalysts:
 - 3. Additives: Pigment, Titanium dioxide
 - 4. Fillers:
- F. Outgassing (Species Characterization):
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - 1. Thermal/Aging: Thermal aging at 250 360° C indicate primary products were N₂, CO and CO₂ (probably resulting from decomposition of NCO groups) as well as phthalates, aromatic amines, phenols and aromatic hydrocarbons (Refs. FOT83A, KAL86A, FOT81A, EID80A, ER180A, LEV80A).
 - 2. Radiation
 - a. Ionizing
 - b. UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products): Phthalates, aromatic amines, phenols and, to a lesser extent, aromatic hydrocarbons.
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 36. Y-966 Adhesive
- B. Specification:
- C. System VCM (g): 0.027
- D. Use: Holds thermal blanket in place.
- E. Chemical Information: Acrylic adhesive.
 - 1. Structure: Acrylic acid monomer.
 - 2. Curing Agent/Hardener/Catalysts: Peroxide and an aromatic amine.
 - Additives:
 - 4. Fillers:
- F. Outgassing (Species Characterization): Major outgassing components are glycol benzoate and monoesters of phthalic acid and such minor components as toulene, H2O, dioctyl phthalate and hydrocarbon oils (MUR67A, GLA82A).
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - Thermal/Aging: At 200°C in vacuum, polymethylmethacrylate loses H₂O with formation of anhydride linkages. Heating above 300 350°C gives rapid decomposition to monomer, CO₂, and volatile hydrocarbons (BOW86A, NEM85A).
 - 2. Radiation
 - a. Ionizing
 - b. UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products):
- I. Radiation Sensitivity (Darkening): Moderate.

- A. Material: 38 Mystic 7453
- B. Specification:
- C. System VCM (g): 0.019
- D. Use: Tape (pressure sensitive)
- E. Chemical Information: Acrylic Adhesive1. Structure: Acrylic acid monomer
 - 2. Curing Agent/Hardener/Catalysts: Benzoyl peroxide and an aromatic amine.
 - 3. Additives:
 - 4. Fillers: Aluminum backing.
- F. Outgassing (Species Characterization): Major outgassing components are glycol benzoate and monoesters of phthalic acid and such minor components as toulene, H₂O, dioctyl phthalate and hydrocarbon oils (MUR67A, GLA82A).
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - Thermal/Aging: At 200°C in vacuum, polymethylmethacrylate loses H₂0 with formation of anhydride linkages. Heating above 300 350°C gives rapid decomposition to monomer, CO₂, and volatile hydrocarbons (BOW86A, NEM85A).
 - 2. Radiation
 - a. Ionizing
 - b. UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products):
- Radiation Sensitivity (Darkening): Moderate.

- A. Material: 41. Eccobond 57C (being replaced by Eccobond 83C)
- B. Specification:
- C. System VCM (g): 0.014
- D. Use: Solder (Electrical connections)
- E. Chemical Information: Conductive Adhesive, Ag
 - 1. Structure: 2-Component Adhesive
 - A. Diglycidyl ether of Bisphenol-A(DGEBA)
 - B. Silver

Ratio of A/B: 20.7% A / 79.2% B

- Curing Agent/Hardener/Catalysts:
- Additives:
- 4. Fillers/Solvents: 10% toulene by wt. for thinning
- F. Outgassing (Species Characterization):
 - GC/MS: Principally H₂O, CO₂, CO, at 25-150°C (Refs. BRO67A, VAS78A, SAN85A).
 - 2. IR
 - 3. 117
 - HPLC/G.P.C.: Low molecular weight phenols from HPLC of Bisphenol-A (Ref. SZA78A).
- G. Degradation/Decomposition:
 - Thermal/Aging: Volatile products included H₂O, CO, CH₃OCH₃, CH₂= CHCH₂OH, CH₂CHCHO, CH₂=CH₂, CH₃CH=CH₂, phenol, substituted phenols, aromatic esters with carbonyls and or ethylenic groups (280°C), (Refs. GRA85A, GRA85B, GRA86A).
 - 2. Radiation
 - a. Ionizing: UV and IR studies of electron irradiated material gave results consistent with thermal/aging studies. Carbonyl and ethylenic bonds were formed, as well as aromatic free radicals (Refs. BUR80A, BUR82A).
 - b. UV: Similar to thermal/aging with addition of $\rm H_2$ and aromatic hydrocarbons (Refs. GRA85C, GRA86B).
 - c. VUV
- H. Summary (Most Probable Outgassing Products): Outgassing products of principle concern with regard to potential radiation darkening are the phenols and substituted aromatic esters and to a lesser extent the carbonyl containing species and unsaturated hydrocarbons.
- I. Radiation Sensitivity (Darkening): Moderate to high.

A. Material: 43. Loctite A

B. Specification:

C. System VCM (g): 0.011

D. Use: Thread Seal

E. Chemical Information: Anaerobic

1. Structure: Polyglycol dimethyacrylates 90 - 95% by wt. Cumene Hydroperoxide 5 - 7% by wt.

Trialkylamine 2 - 3% by wt.

- 2. Curing Agent/Hardener/Catalysts: Cumene Hydroperoxide, trialkylamine.
- 3. Additives:
- 4. Fillers:
- F. Outgassing (Species Characterization): Major outgassing components are glycol benzoate and monoesters of phthalic acid and such minor components as toulene, H₂O, dioctyl phthalate and hydrocarbon oils (MUR67A, GLA82A).
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - Thermal/Aging: At 200°C in vacuum, polymethylmethacrylate loses H₂0
 with formation of anhydride linkages. Heating above 300 350°C gives rapid decomposition to monomer, CO₂, and volatile hydrocarbons (BOW86A, NEM85A).
 - 2. Radiation
 - a. Ionizing
 - b. UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products):
- I. Radiation Sensitivity (Darkening): Moderate.

- A. Material: 45. Epon 825HV
- B. Specification:
- C. System VCM (g): 0.006
- D. Use: Electrical casting, encapsulation, specialized tooling.
- E. Chemical Information: Epoxy resin
 - 1. Structure Diglycidyl ether of Bisphenol-A(DGEBA)
 - 2. Curing Agent/Hardener/Catalysts: Aliphatic amine
 - Additives:
 - 4. Fillers:
- F. Outgassing (Species Characterization):
 - GC/MS: Principally H₂O, CO₂, CO, at 25-150°C (Refs. BRO67A, VAS78A, SAN85A).
 - 2. IR
 - 3. UV
 - HPLC/G.P.C.: Low molecular weight phenols from HPLC of Bisphenol-A (Ref. SZA78A).
- G. Degradation/Decomposition:
 - Thermal/Aging: Volatile products included H₂O, CO, CH₃OCH₃, CH₂= CHCH₂OH, CH₂CHCHO, CH₂=CH₂, CH₃CH=CH₂, phenol, substituted phenols, aromatic esters with carbonyls and or ethylenic groups (280°C), (Refs. GRA85A, GRA85B, GRA86A).
 - 2. Radiation
 - a. Ionizing: UV and IR studies of electron irradiated material gave results consistent with thermal/aging studies. Carbonyl and ethylenic bonds were formed, as well as aromatic free radicals (Refs. BUR80A, BUR82A).
 - b. UV: Similar to thermal/aging with addition of $\rm H_2$ and aromatic hydrocarbons (Refs. GRA85C, GRA86B).
 - c. VUV
- H. Summary (Most Probable Outgassing Products): Outgassing products of principle concern with regard to potential radiation darkening are the phenols and substituted aromatic esters and to a lesser extent the carbonyl containing species and unsaturated hydrocarbons.
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 50. Urethane Insulation
- B. Specification: J-W-1177 cl 130/General (INT. Fed. Specif.)
- C. System VCM (g): 0.003
- D. Use: Electrical magnet wire
- E. Chemical Information: Polyurethane/nylon coating
 - 1. Structure
 - 2. Curing Agent/Hardener/Catalysts:
 - 3. Additives:
 - 4. Fillers:
- F. Outgassing (Species Characterization):
 - 1. GC/MS
 - 2. IR ----
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - L. Thermal/Aging: Thermal aging at $250 360^{\circ}$ indicate primary products were N_2 , CO and CO₂ (probably resulting from decomposition of NCO groups) as well as phthalates, aromatic amines, phenols and aromatic hydrocarbons (Refs. FOT83A, KAL86A, FOT81A, EID80A, ER180A, LEV80A).
 - 2. Radiation
 - a. Ionizing
 - ъ. UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products): Phthalates, aromatic amines, phenols and, to a lesser extent, aromatic hydrocarbons.
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 51. Tape 3M 1318
- B. Specification: MIL-I-15126MFT
- C. System VCM (g): 0.003
- D. Use: Electrical insulation; internal coil application
- E. Chemical Information: Polyester film
 - Structure: Polyethylene Terephthalate (PET).
 - 2. Curing Agent/Hardener/Catalysts:
 - Additives:
 - 4. Fillers:
- F. Outgassing (Species Characterization):
 - GC/MS: Phthalates, in particular, di-2-ethylhexyl phthalate (COL72A, COL76A, COL79B)
 - 2. IR: Extraction of polymer in organic solvents indicated presence of cyclic trimer as well as other oligomers (ADA82A).
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - 1. Thermal/Aging: Main Chain scission of the ester links, accompanied by decarboxylation and formation of CO, CO₂, acetaldehyde, aromatic acids and vinyl esters (BED81A, ADA82A, ING82A, SUE84A, OHT86A).
 - 2. Radiation
 - a. Ionizing: Chain scission and crosslinking indicative of main chain rupture (HAN69A, BEL83A).
 - b. UV: Photochemical yields of CO (and CO₂) as well as COOH end groups indicate main chain scission as the dominant process (DAY71A, WIL73A, ILI85A).
 - c. VUV: Yields of CO and CO₂, and decrease in the oxygen to carbon ratio suggest that main chain scission with decarboxylation is major degradation made (LAZ86A).
- H. Summary (Most Probable Outgassing Products): All of the above evidence points to monomers, dimers, trimers and other low molecular weight oligomers as the chief expected outgassing products. Thus low molecular weight phthalates, which are among the most common outgassing products found in spacecraft sampling (COL79B) are the most likely species of concern with regard to potential radiation induced darkening. Indeed, at low temperatures, highly colored, stabilized ionic species have been observed (TOR85A).
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 52. PR1440 Polysul
- B. Specification:

Also: MIL-S-8802, ClA and ClB

- C. System VCM (g): 0.003
- D. Use: Fuel tank sealant (with or without protective top coat).
- E. Chemical Information:
 - 1. Structure: Mercaptan terminated long chain aliphatic polymer containing disulfide linkages.
 - A. Polysulfide.

Mix Ratio: 11:1 by weight (Base compound to accelerator)

- Curing Agent/Hardener/Catalysts: B. Accelerator (contains Pb): MnO, PbO₂, Dichromates or org. free radicals.
- Additives:
- 4. Fillers: Silicon dioxide (325 mesh).
- Outgassing (Species Characterization):
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- 3. Degradation/Decomposition:
 - 1. Thermal/Aging: Thermal decomposition studies (RAO85A, RAD86A) yield a wide variety of cyclic low molecular wieght compounds. The nature of the products observed suggests rupture of C-O, C-S, and S-S bonds all occuring to an appreciated degree.
 - 2. Radiation
 - a. Ionizing
 - b. UV
 - c. VUV
- . Summary (Most Probable Outgassing Products):
 Most likely outgassing products are likely to be low molecular weight monomers, dimers, etc. of the parent species. Although some evidence for crosslinking or aging has been observed (DAV84A), the nature of the most probable outgassing products suggests that bond rupture to form lower molecular weight (more volatile) species will be the dominant degradation made and that radiation or photochemical induced polymerization, ionization or other process yielding darkened material will be a minor reaction pathway.
- I. Radiation Sensitivity (Darkening): Low to moderate.

- A. Material: 53. Mylar Sleeving
- B. Specification: MIL-I-23053/7B
- C. System VCM (g): 0.003
- D. Use: Insulation Sleeving, heat shrinkable, non-crosslinked.
- E. Chemical Information: Polyester
 - 1. Structure: Polyethylene Terephthalate (PET)
 - 2. Curing Agent/Hardener/Catalysts:
 - 3. Additives:
 - 4. Fillers:
- F. Outgassing (Species Characterization):
 - GC/MS: Phthalates, in particular, di-2-ethylhexyl phthalate (COL72A, COL76A, COL79B)
 - 2. IR: Extraction of polymer in organic solvents indicated presence of cyclic trimer as well as other oligomers (ADA82A).
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - Thermal/Aging: Main Chain scission of the ester links, accompanied by decarboxylation and formation of CO, CO₂, acetaldehyde, aromatic acids and vinyl esters (BED81A, ADA82A, ING82A, SUE84A, OHT86A).
 - 2. Radiation
 - a. Ionizing: Chain scission and crosslinking indicative of main chain rupture (HAN69A, BEL83A).
 - b. UV: Photochemical yields of CO (and CO₂) as well as COOH end groups indicate main chain scission as the dominant process (DAY71A, WIL73A,ILI85A).
 - c. VUV: Yields of CO and ${\rm CO}_2$, and decrease in the oxygen to carbon ratio suggest that main chain scission with decarboxylation is major degradation made (LAZ86A).
- H. Summary (Most Probable Outgassing Products): All of the above evidence points to monomers, dimers, trimers and other low molecular weight oligomers as the chief expected outgassing products. Thus low molecular weight phthalates, which are among the most common outgassing products found in spacecraft sampling (COL79B) are the most likely species of concern with regard to potential radiation induced darkening. Indeed, at low temperatures, highly colored, stabilized ionic species have been observed (TOR85A).
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 54. Tape 3M 415
- B. Specification:
- C. System VCM (g): 0.002
- D. Use:
- E. Chemical Information: Polyester film
 - 1. Structure: Polyethylene Terephthalate (PET).
 - 2. Curing Agent/Hardener/Catalysts:
 - 3. Additives:
 - 4. Fillers:
- F. Outgassing (Species Characterization):
 - 1. GC/MS: Phthalates, in particular, di-2-ethylhexyl phthalate (COL72A, COL76A, COL79B)
 - 2. IR: Extraction of polymer in organic solvents indicated presence of cyclic trimer as well as other oligomers (ADA82A).
 - 3. UV
 - HPLC/G.P.C.
- G. Degradation/Decomposition:
 - Thermal/Aging: Main Chain scission of the ester links, accompanied by decarboxylation and formation of CO, CO₂, acetaldehyde, aromatic acids and vinyl esters (BED81A, ADA82A, ING82A, SUE84A, OHT86A).
 - 2. Radiation
 - a. Ionizing: Chain scission and crosslinking indicative of main chain rupture (HAN69A, BEL83A).
 - b. UV: Photochemical yields of CO (and CO₂) as well as COOH end groups indicate main chain scission as the dominant process (DAY71A, WIL73A, ILI85A).
 - c. VUV: Yields of CO and ${\rm CO}_2$, and decrease in the oxygen to carbon ratio suggest that main chain scission with decarboxylation is major degradation made (LAZ86A).
- H. Summary (Most Probable Outgassing Products): All of the above evidence points to monomers, dimers, trimers and other low molecular weight oligomers as the chief expected outgassing products. Thus low molecular weight phthalates, which are among the most common outgassing products found in spacecraft sampling (COL79B) are the most likely species of concern with regard to potential radiation induced darkening. Indeed, at low temperatures, highly colored, stabilized ionic species have been observed (TOR85A).
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 55. Tape 3M27
- B. Specification: MIL-I-15126FGFT
- C. System VCM (g): 0.002
- D. Use: Electrical insulation; Construction and repair of elec./electronic equipment.
- E. Chemical Information: Polyester
 - 1. Structure: Polyethylene Terephthalate (PET)
 - Curing Agent/Hardener/Catalysts:
 - 3. Additives:
 - 4. Fillers: Glass fabric backing
- F. Outgassing (Species Characterization):
 - GC/MS: Phthalates, in particular, di-2-ethylhexyl phthalate (COL72A, COL76A, COL79B)
 - 2. IR: Extraction of polymer in organic solvents indicated presence of cyclic trimer as well as other oligomers (ADA82A).
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - Thermal/Aging: Main Chain scission of the ester links, accompanied by decarboxylation and formation of CO, CO₂, acetaldehyde, aromatic acids and vinyl esters (BED81A, ADA82A, ING82A, SUE84A, OHT86A).
 - 2. Radiation
 - a. Ionizing: Chain scission and crosslinking indicative of main chain rupture (HAN69A, BEL83A).
 - b. UV: Photochemical yields of CO (and CO₂) as well as COOH end groups indicate main chain scission as the dominant process (DAY71A, WIL73A,ILI85A).
 - c. VUV: Yields of CO and ${\rm CO}_2$, and decrease in the oxygen to carbon ratio suggest that main chain scission with decarboxylation is major degradation made (LAZ86A).
- H. Summary (Most Probable Outgassing Products): All of the above evidence points to monomers, dimers, trimers and other low molecular weight oligomers as the chief expected outgassing products. Thus low molecular weight phthalates, which are among the most common outgassing products found in spacecraft sampling (COL79B) are the most likely species of concern with regard to potential radiation induced darkening. Indeed, at low temperatures, highly colored, stabilized ionic species have been observed (TOR85A).
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 56. Anodize
- B. Specification: MIL-A-8625 Ty II
- C. System VCM (g): 0.002
- D. Use: Anodic coating for aluminum and aluminum alloys.
- E. Chemical Information: Al, electrolytically coated
 - 1. Structure
 - 2. Curing Agent/Hardener/Catalysts:
 - 3. Additives: Sulfuric acid bath (to produce a uniform coating); completely sealed.
 - 4. Fillers:
- F. Outgassing (Species Characterization):
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:

- A. Material: 58. Polyimide Film
- B. Specification: MIL-P-46112
- C. System VCM (g): 0.001
- D. Use:
- E. Chemical Information: Polyimide
 - 1. Structure
 - 2. Curing Agent/Hardener/Catalysts:
 - 3. Additives:
 - 4. Fillers:
- F. Outgassing (Species Characterization):
 - 1. GC/MS:
 - 2. IR
 - 3. UV:
- 4. HPLC/G.P.C.
- G. Degradation/Decomposition: H₂O Sensitive.
 - 1. Thermal/Aging: Although little chemical information is available, weight and property measurements indicate that at high temperatures this material is extremely stable to thermal aging (Ref. SRO 65A).
 - 2. Radiation Polymers of this type (polybenzimidizole) are among the most radiation resistant polymers known. Low dose rate electron irradiation produces rupture of the aromatic ether linkage in the molecule (REF FER 81A).
 - a. Ionizing
 - b. UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products):

The thermal and radiation aging results given above suggest this material will outgas monomer, dimer and other low molecular weight olegomers on aging, but at very slow rates. While the latter appears favorable from a contamination point of view, it must be remembered that these materials, even before irradiation, typically absorb strongly in the uv and even into the visible regions of the solar spectrum, and darken even more with irradiation. The high system VCM for Kapton belies the inherent stability of this polymer. If the VCM is due to solvent outgassing, the typical solvents used in preparation of the material pose low to moderate darkening concerns; if, however, the system VCM is due to monomer outgassing, moderate to high concerns exist. This point should be checked.

I. Radiation Sensitivity (Darkening):

Low to high.

- A. Material: 59. Epon 828HV
- B. Specification:
- C. System VCM (g): 0.006
- D. Use: Electrical encapsulants and laminants
- E. Chemical Information: Epoxy resin
 - 1. Structure: Diglycidyl ether of Bisphenol-A(DGEBA)
 - Curing Agent/Hardener/Catalysts: Aliphatic amine (triethylene tetramine, TETA; Diethylene triamine, DETA etc)
 - 3. Additives:
 - 4. Fillers: Inert filler for shrinkage (? calcium carbonate)
 - . Outgassing (Species Characterization):
 - GC/MS: Principally H₂O, CO₂, CO, at 25-150°C (Refs. BR067A, VAS78A, SAN85A).
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.: Low molecular weight phenols from HPLC of Bisphenol-A (Ref. SZA78A).
- Degradation/Decomposition:
 - Thermal/Aging: Volatile products included H₂O, CO, CH₃OCH₃, CH₂= CHCH₂OH, CH₂CHCHO, CH₂=CH₂, CH₃CH=CH₂, phenol, substituted phenols, aromatic esters with carbonyls and or ethylenic groups (280°C), (Refs. GRA85A, GRA85B, GRA86A).
 - 2. Radiation
 - a. Ionizing: UV and IR studies of electron irradiated material gave results consistent with thermal/aging studies. Carbonyl and ethylenic bonds were formed, as well as aromatic free radicals (Refs. BUR80A, BUR82A).
 - b. UV: Similar to thermal/aging with addition of $\rm H_2$ and aromatic hydrocarbons (Refs. GRA85C, GRA86B).
 - c. VUV
- H. Summary (Most Probable Outgassing Products): Outgassing products of principle concern with regard to potential radiation darkening are the phenols and substituted aromatic esters and to a lesser extent the carbonyl containing species and unsaturated hydrocarbons.
- I. Radiation Sensitivity (Darkening): Moderate to high.

- A. Material: 79. Chemglaze Z306
- B. Specification:
- C. System VCM (g): 0.000
- D. Use: Paint (flat black)
- E. Chemical Information:
 - 1. Structure
 - 2. Curing Agent/Hardener/Catalysts:
 - 3. Additives:
 - 4. Fillers:
- F. Outgassing (Species Characterization):
 - 1. GC/MS
 - 2. IR
 - 3. UV
 - 4. HPLC/G.P.C.
- G. Degradation/Decomposition:
 - Thermal/Aging: Thermal aging at 250 360°C indicate primary products were N₂, CO and CO₂ (probably resulting from decomposition of NCO groups) as well as phthalates, aromatic amines, phenols and aromatic hydrocarbons (Refs. FOT83A, KAL86A, FOT81A, EID80A, ERI80A, LEV80A).
 - 2. Radiation
 - a. Ionizing
 - b. UV
 - c. VUV
- H. Summary (Most Probable Outgassing Products): Phthalates, aromatic amines, phenols and, to a lesser extent, aromatic hydrocarbons.
- I. Radiation Sensitivity (Darkening): Moderate to high.

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